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Editor-in-Chief
Vladimir N. Kholodov

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A Journal on Problems of the Theory of
Sedimentary Rock Formation and Ore Genesis



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Lithology and Mineral Resources

(*Litologiya i Poleznye Iskopaemye*)

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Editor-in-Chief

Vladimir N. Kholodov

Academician of the Academy of Natural Sciences,
Professor, Dr. Sci. (Geol.-Miner.)

Address for correspondence:

Litologiya i Poleznye Iskopaemye, Geological Institute (GIN), Russian Academy of Sciences,
Pyzhevskii per. 7, Moscow, 109017 Russia
Phone: 230-80-09; E-mail: kholodov@ginran.msk.su

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Lithology and Mineral Resources (Litologiya i Poleznye Iskopaemye) reviews a wide range of problems related to the formation of sedimentary rocks and ores. Special attention is devoted to comparison of ancient sedimentary rock and ore formation with present-day processes, as the idea of actualism has always constituted one of the bases of the scientific philosophy of lithologists. A major part of the journal is devoted to comparative analysis of sedimentary processes on continents and in oceans, as well as the genetic aspects of the formation of sedimentary and hydrothermal-sedimentary mineral resources. The journal was founded in 1963 by Academician N. M. Strakhov. It will be of interest to lithologists, petrographers, geochemists, mineralogists, ore geologists and metallogenists, as well as to other geologists, ecologists, researchers of experimental and analytical laboratories, and graduate students.

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Academy of Sciences and the Progress of Lithology (275th Anniversary of the Russian Academy of Sciences)

V. N. Kholodov

Geological Institute, Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 109017 Russia

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The history of the Russian Academy of Sciences is mostly the history of the native geological science. During the 18th century, the academy was the only scientific institution that concentrated most scientific work in Russia. Later, throughout the 19th century and until 1917, the academy ceased to be monopolist in the scientific activity of the country but still remained a center of the Russian scientific ideas. At that time, the lithology or the science dealing with sedimentary rocks and ores was only an embryonal state within geology, mineralogy, and petrography; it has not yet existed as a discipline in its own right.

The origination of lithology in Russia is related to the post-revolutionary period. In 1922, M.S. Shvetsov (Moscow Mining Academy), B.P. Krotov (Kazan State University), and D.V. Nalivkin (St. Petersburg University) pioneered the delivering of courses devoted to sediments, sedimentary rocks, and ores. The study on regularities of the sedimentary process was a major preoccupation of academicians A.P. Pavlov, N.A. Andrusov, A.D. Arkhangel'skii, V.I. Vernadskii, I.M. Gubkin, A.E. Fersman, A.P. Karpinskii, A.P. Vinogradov, N.M. Strakhov, P.I. Stepanov, Yu.A. Zhemchuzhnikov, N.S. Shatskii, N.S. Kurnakov, A.V. Sidorenko, A.B. Ronov, A.L. Yanshin, V.I. Smirnov, A.P. Lisitsyn, and others.

After the Russian Revolution, the lithologic ideas were long confined to studying sedimentary mineral resources of central regions, the Urals, Caucasus, and Kola Peninsula. Later, after the 1920s, the reorganization of the Academy of Sciences, the establishment of academies of union republics, the setting up of the Siberian Branch, Far East and Urals scientific centers, the establishing of the Bashkiria, Dagestan, Kazan, Kola, and Komi branches of the Academy of Sciences substantially enlarged the geography of lithologic investigations and undoubtedly assisted the refining of the lithologic theory.

It was just at that time that the lithology appeared and formed as an independent branch of geological sciences; the Russian academic institutions played an important part in its origin and progress.

I

On January 22, 1724, Peter the Great examined the draft regulations for the Academy of Sciences and its University. The academy was regarded as "an assembly of scientists and skillful people who are eager to implement and augment these sciences in their kind, degree, and through new inventions."

L.L. Blumentrost, a physician, was appointed first president of the Academy of Sciences and Arts; such prominent foreign scientists as mathematicians, Ya. Hermann, H. Goldbach, L. Euler, N. Bernoulli and D. Bernoulli, physicists G. Bulfinger, G.V. Kraft, astronomer J.N. Delisle, optician and mechanic I.G. Leitmann, naturalists I. Duvernois, I. Weitbrecht, I.G. Gmelin were invited as members of the academy. L. Euler and D. Bernoulli, world-renowned mathematicians, brought a profound pride to the academy.

According to the Senate decree dated January 28, 1724, customs' profits of 22912 rubles in gold gained from the cities Derpt, Narva, and Arensburg were granted to the Imperial Academy as running costs to support the academy. The academy received the library at its disposal, which stored manuscripts of the Russian tsars, private books of Peter the Great, collections of books bought from A.A. Vinus and confiscated from the physician-in-ordinary R. Areskin, as well as the *Kunstkammera* (curiosity room) that comprised a splendid collection of rarities among which the collection of "Ores and Stones Found in Russia" occupied a highly important place.

The opening ceremony in the Academy of Sciences and Arts took place in the reign of Katherine I after Peter the Great had passed away on August 1, 1726, though the regulations for the academy were approved a year before. Several buildings on Vasilievskii Island were placed at the academy's disposal in St. Petersburg. In addition to the library and curiosity room, the academy had from the outset a printing house, observatory, physical center, dissecting-room, botanical garden, tool workshops, engraving and drawing chambers, and some other auxiliary institutions.

Eighty-four persons were on the list of the academy in 1727; there were 17 professors-academicians, 1 junior scientific assistant, 11 students, 7 interpreters,

10 clerks, and 38 service personnel. It is worthy to note that no Russians were available among academicians; the Germans were dominating among the professors.

Concurrent with the establishment, the publishing activity of the Imperial Academy got under way. The draft regulations said that "every academician is obliged to read works of good authors of its own science which are published in foreign countries. In doing so, it will be easy for him to extract necessary information. Such extraction along with inventions and reasoning are to be published by the academy in the prescribed time."

From April 1728, more appreciable works of academicians are published in *Kommentarii*; from 1728 to 1751, fourteen volumes were published in the Latin, Russian and German languages. Issued among periodicals of the academy are the newspaper *Sankt-Peterburgskie vedomosti*, the popular-scientific journal *Primechaniya k Sankt-Peterburgskim vedomostyam*, and yearly calendars.

Primechaniya... was very important in the popularization of geology; most anonymously written articles of interest by the academicians were published: *On the Metallurgy or Mining Science*, *On the Stone Asbestos and Fabrics Made From That Stone*, *On the Phosphorus*, *On Amber*, *Physical News about Healing Water in General*, *On Marine Shells and Other Things Dug out of the Earth*, *On Oil*, *On Mammoth's Bones*, and *On Discovery of America and Migration of Europeans into It*. In the papers devoted to earthquakes, the appearance of comets, Aurora Borealis, and so on, the phenomena were scientifically explained, and their interpretation as forerunners of various calamities were disproved.

Judging by the materials from *Primechaniya*, academicians L. Euler and I. Weitbrecht, adjunct G.V. Richtman, as well as the Russian scientists V.N. Tatishchev and I.K. Kirillov were the first to popularize geology and mineralogy in Russia. Among them, the great Russian scientist M.V. Lomonosov stands out. He was elected adjunct of the academy in 1742 and professor in 1745.

Lomonosov's activity was very versatile; he took up physics, metallurgy, mining, geology, history, astronomy, art, and poetry. Among his geological works, there were *Dissertation on the Origin and Nature of Nitre* (1779), *Reflections on the Causes of Heat and Cold* (1750), *A Word about the Origin of Metals Due to Earthquakes* (1757), *Pioneering Works in Metallurgy or Mining* (1763) with a supplement *On the Earth's Layers*.

Of fundamental importance in the works is the fact that the Earth's evolution was assumed as a successive process. He wrote: "the Earth's surface is quite different at present as compared to that in old times." Being aware of the immense continuance of the geologic time, Lomonosov boldly disproved the attempts to put geochronology into the framework of biblical chronology.

The second peculiar feature of Lomonosov's works is a deliberate use of the actualistic method, i.e., interpretation of phenomena of the geologic past by the means of comparison with modern processes. According to the actualistic approach, Lomonosov has managed to correctly explain the origin of peat, coal, and amber, convincingly substantiating the phylogenous nature of these substances. Lomonosov was the first who subdivided the geological processes into exogenic (wind, rainfall, river, sea water, flood activities) and endogenic (slow and fast fluctuations of the earth surface, volcanic activity), and described the alternation of sea transgressions and regressions.

Problems of the genesis of sedimentary rocks occupied an important place in Lomonosov's works. He showed how disintegration of massive rocks occurred under the effect of superficial forces to form sand. He also denoted several modes of sedimentary rock origin: (1) consolidation of from clay, (2) injection of viscous liquid material, (3) accumulation and consolidation, (4) coagulation, and (5) granulation.

Lomonosov's assumptions on the role of natural water and organisms in formation of some minerals, ores, and rocks were the pioneer ideas in geology. Geological treatises of Lomonosov stood much higher than the works of his contemporaries and anticipated the ensuing achievements in science.

Lomonosov was not only a genius scientist; he was a great organizer of science, and the history of the Academy of Sciences from 1742 to 1765 was connected with his name. Baron K.G. Keizerling, Baron I.A. Korf, Count K.G. Razumovskii, Count V.G. Orlov as well as the subordinates I. Shumakher, I.G. Lestok, G.N. Teplov, all who were successively nominated the director or president of the academy, were striving to make the academy one of the bureaucratic institutions of the empire, to centralize power (authority), to strengthen the importance of foreign scientists, and to present them maximal privileges in science. Immediately after joining the academy, Lomonosov was at the forefront of the struggle of Russian scientists against a one-man management of the reactionary academic clique.

Lomonosov elaborated a draft of new and more democratic regulations of the academy; he took an active part in the activity of the academic university and gymnasium, delivered lectures, and worked out new programs for teaching students. Moscow University, the oldest in Russia, was initiated by him during the reign of Tsarina Elizaveta and opened in 1755. In 1759, by solicitation of Lomonosov, a new category of workers appeared in the academy; they became corresponding members. Assigned to them were those who "have not enough knowledge to be a member but still can serve the academy with proceedings and transactions." Lomonosov gave much attention to the management of geologic-geographic and economic studies of the

country after taking charge of the office of the Academy of Sciences.

At the turn of the 18th century in Russia, there was a period of famous academic expeditions organized under Lomonosov's project and headed by his apprentices and disciples. Among the leaders of the earliest academic expeditions, one can encounter the names of academicians I.I. Lepekhin, N.Ya. Ozeretskovskii, S.P. Krasheninnikov, I.S. Pallas, V.F. Zuev, S.G. Gmelin, I.A. Gil'denshtedt, I.G. Georg, and many others.

The Orenburg Expedition headed by Lepekhin (1768) explored both sides of the Volga region, the Urals, and the Arkhangel'sk province. Alongside with the description of nature, Lepekhin's works comprise numerous conclusions on "various changes of the globe," on the replacement of land by sea and vice versa, and on transformation of ridges into valleys. The scientist proved that fossils were not a freak of nature but were remains of older animals and struggled against the idea of the Deluge that was popular in the 18th century.

Expeditions headed by Pallas (1773–1788) embraced the area from St. Petersburg to the Caspian Sea, as well as the area of southern Siberia from the Urals to the Transbaikal region. He concluded that Obshchii Syrt and Ergeni represent ancient shores of the Caspian Sea. In Pallas's opinion, the Caspian Sea level was higher in the past, and the sea was communicating with the Black Sea until straits connecting the Black and Mediterranean seas were formed. The Black Sea level gradually lowered, and it separated from the Caspian Sea; in a similar manner, the Aral Sea separated from the Pontian basin. The work of Pallas was a pioneer study in the paleogeography of Russia, which was corroborated by succeeding investigations. Later, Pallas described mud volcanoes of Kerch Peninsula, salt deposits of Crimean lakes, the formation of sand banks, as well as sedimentary rocks of Crimean Mountains.

The expedition headed by Gmelin (1773) entered the territory of Azerbaijan, under the Persian sovereignty, and collected information on oil sources on the Apsheron Peninsula. Gildenshtedt was the first who described "black soil" in the Kura and Rioni river valleys and attributed soil formation to the decay of perished vegetation; later his ideas formed the basis of the soil science.

The importance of great academic expeditions is difficult to overestimate; they substantially aroused interest in studying natural resources of Russia, augmented mineralogical collections of the *Kunstkamera*, and contributed to conceiving the early scientific ideas on the sedimentary soil formation. Transactions of the Academy of Sciences, namely, *Novi Commentarie, Acta, Nova Acta* as well as journal *Akademicheskie izvestiya*, were popular in the late 1790s, not only in Russia but abroad as well.

At the same time, hardships during the expeditions could not be belittled. A shortage of food, instruments, and money, as well as dangerous epidemic diseases, suspiciousness of native population, and the lack of transport imposed severe trials upon the health and fortitude of researchers. It was well known that two of them, Gmelin and Falk, have tragically died in the expedition.

II

During the 19th century, the Academy of Sciences was gradually losing its position as the only center of scientific ideas in Russia. Institutes are established at a rapid pace in various cities of the country. Yuriev University was founded under the reign of Tsar Aleksandr I in 1802, Kazan and Kharkov universities in 1804, St. Petersburg University in 1819, and Kiev University in the time of Tsar Nikolai I in 1833, which was originally named after St. Vladimir.

The university regulations of 1804 conceded wide democratic rights to universities; a heart of them being councils of professors from which a rector and deans were elected. The councils approved teaching plans, examination schedules, awarded degrees and gave new assignments.

Later, the plot of Decembrists changed the situation with higher educational institutions in Russia; in 1835, new regulations were adopted under the pressure of M.L. Magnitskii and D.P. Runich; a trustee appointed by authorities became the head of a university, the rights of the councils got curtailed, rectors and deans were appointed for shorter terms, and students were imposed the duty of wearing a uniform.

A struggle for the university liberties continued until the reign of Aleksandr II; under this emperor, a number of universities was established—Novorossiisk in 1864, Warsaw in 1869, Tomsk in 1880—and a new reform was implemented for universities. All restrictive measures had been cancelled, and a complete autonomy of the corporation of professors became a principal idea of the regulations of 1864.

The status of higher educational institutions in Russia essentially changed in 1884 when new regulations were adopted under the reign of Aleksandr III. According to them, the Ministry of Education of Russia had the right to appoint rectors, deans, and professors on the basis of representations made by a commission of officials. Admittance to universities was reduced especially for non-Russian students, primarily Poles and Jews.

Different clubs, societies, and associations of scientists, in which lithologic problems were often discussed in addition to other geological issues, were established at the universities in the 19th century. In 1804, the Society of Naturalists was established at Moscow University, and the Mineralogical Society began to work in Petersburg in 1817.

Foundation of the Geological Committee (Geolkom) in 1882 was a great event in the geological life of Russia; Academician G.P. Gelmersen was appointed as the first director. Naturally, the geological studies carried out by the academy looked very modest against the background of geological mapping conducted by the Geolkom over the entire territory of the country in the late 19th–early 20th centuries.

Methods of work of the Emperor Academy substantially changed in the early 19th century. The epoch of comprehensive, natural–historic academic expeditions ended by that time. The mining industry, then in progress, required systematic studies of some regions of the country. According to new regulations adopted by the Emperor Academy in 1803, the academy should develop sciences with perspectives of new discoveries, as well as extend education and take care of practical implementation. The number of academicians increased to 18. Each academician had an adjunct. Academicians, adjuncts, honored members, and corresponding members made up the academic assembly. When electing academicians, Russian scientists were preferred over the foreign ones.

The president of the academy was nominated by the tsar. Presidents during the period from 1803 to 1917 included N.N. Novosil'tsev, Count S.S. Uvarov, Count D.N. Bludov, Count D.A. Tolstoi, Count F.P. Litke, and Grand Duke K.K. Romanov. According to the regulations, the academy comprised a library; a room of models and rarities; a museum of botany, zoology, and mineralogy; an astronomical observatory; a physical study; a collection of medals; a dissecting room; chemical laboratories; a botanical garden; a printing house; a book store; and academic archives.

In 1841, the Russian Academy temporarily joined the Emperor Academy, and famous Russian writers I.A. Krylov, V.A. Zhukovskii, P.A. Vyazemskii and others appeared among the academicians.

Academician V.M. Severgin was a prominent mineralogist at the threshold between the 18th and 19th century. In his fundamental works *Pioneer Principles of Mineralogy* (1798) and *Mineralogical Dictionary* (1807), Severgin presented thorough reviews of the state-of-the-art mineralogical data. Long before I.F. Breitaupt, he formulated a notion of the paragenesis ("contiguity") of minerals, drew some important inferences about the origin of erratic boulders, and described the genesis of salt deposits and basalts. In accordance with Lomonosov's precepts, Severgin issued in 1809 the *Experience of Mineralogical Description in the Russian State*, the pioneer work in the topographic mineralogy. After Severgin had passed away, his studies were continued by academician N.I. Koksharov.

Academicians K.M. Baer and G.V. Abich contributed much to geology, but works by academician G.P. Gelmersen merit special notice. Geological expeditions headed by Gelmersen embraced the territory from the Olonets province to the Black Sea as well as

from the Altai and the Urals to the Baltic Sea coast. In 1841, he compiled the first geologic map of the Russian Platform in which nine stratigraphic units were distinguished. Later, Gelmersen elaborated the methods of the geological mapping and supervised the compilation of the geological map of Russia in the Geolkom. In the academy, coal deposits were a major preoccupation of Gelmersen; he studied the coal geology of the Moscow and Donetsk basins, the Dombrovsk basin in Poland, and the coal potential in the Urals and Ukraine. The study of Donetsk coal fields commenced by Gelmersen was later continued by L.I. Lutugin who took charge of a large group of young enthusiasts-geologists.

At about the same time, fundamental works by academician V.V. Dokuchaev on the origin of soil were published. In his principal work *The Russian Chernozem* (1883), Dokuchaev proposed two basic ideas: (1) about the geographic, zoned distribution of soils in close relation to their genesis; (2) about soil as a peculiar natural body, the result of interaction of climate, host rocks, vegetation, and animals. The foundation for the modern soil science was laid in Dokuchaev's works. His disciples, academicians K.D. Glinka, N.M. Sibirtsev, G.I. Vysotskii, and many others developed soil science pedology to a discipline.

The works by A.P. Karpinskii on petrography, paleontology, tectonics, and especially paleogeography made an outstanding contribution to geology. To reveal the history of the European part of Russia, Karpinskii pioneered in applying the method of the facies analysis. He proved that the Carboniferous deposits of the Moscow region and Donetsk basin differ radically in the petrographic composition due to various paleodepositional conditions. Karpinskii offered a sophisticated analysis of the Russian Platform structure and depicted a captivating picture of its evolution in several papers published in 1919 and in the book *Outlines of geological past of the European Russia*. It was revealed that oscillating motion of the basement blocks of the platform had a long-term influence on depositional conditions of the Phanerozoic rocks. During some geological periods, the basement submerged in the latitudinal direction, whereas in other stages, the basement submerged in the meridional; as a result, seas periodically covered the Russian Platform variously in latitudinal or meridional strips. Therefore, some seas appeared to be parallel to the Urals, whereas others subparallel to the Caucasus. Studies of present-day geologists, who are equipped with deep sea drilling data, confirmed most inferences made by Karpinskii.

The Geological Museum was the heart of mineralogical studies carried out in the academy; F.N. Chernyshev, who contributed much force and energy to this institution, was appointed director in 1900.

E.S. Fedorov, adjunct of the academy, developed an extremely important line in the field of mineralogy. He elaborated a methodical basis for microscopy of minerals in *Principles of Figures* (1885), *Outlines of Ana-*

tomical Crystallography (1887), *Symmetry of Regular Systems of Figures* (1890), *The Theory of Crystallographic Structure* (1905), and other works. His fundamental work *A Kingdom of Crystals* and numerous crystallography courses allowed the development of a new classification of minerals, including the classification of minerals of sedimentary rocks. Later, when studying rocks of the Urals, Fedorov analyzed processes of metamorphism more thoroughly and characterized the chronological sequence of mineral associations.

The establishment of the genetic mineralogy is related to the scientific activity of academician V.I. Vernadskii, Dokuchaev's disciple. He was the first who perceived minerals as products of chemical processes occurring in the Earth's crust. The theory of the aluminosilicate structure and studies on isomorphism of elements in minerals were the acme of Vernadskii's research in mineralogy. Le Chatelier credited Vernadskii's views on the chemical nature of aluminosilicates as a "great hypothesis."

Vernadskii's fundamental work *Experience of Descriptive Mineralogy* is particularly significant. When creating the work, the scientist reconsidered mineralogy in the context of genesis of minerals. Special attention in the work was given to the role of the human activity in the mineral formation. In addition, Vernadskii strove for establishing a comprehensive topographic mineralogy in Russia.

Starting in 1910, Vernadskii was engaged in studies into the mineralogy and geochemistry of elements, especially rare and radioactive, in the territory of Russia; along with his students (A.E. Fersman, Ya.V. Samoilov, K.A. Nenadkevich, *et al.*), Vernadskii carried out a systematic study of the history of chemical elements in the Earth's evolution and set up a new science (geochemistry).

Works by academician N.I. Andrusov were important in the build up of lithology; he applied the comparative-lithologic method for reconstructing the formation conditions of the Tertiary sequences in the Caucasus and Crimea, and was the first who regularly studied recent sediments of the Black and Caspian seas. He examined the composition of bottom silt, the gas regime of bottom water, the origin of fauna and its occurrence in epicontinental seas of southern Russia in *Problems of the Study of the Black Sea and Adjacent Countries* (1893, 1894), *Bosphorus and Dardanelles* (1905), *Outline of the History of the Caspian Sea and its Inhabitants* (1889), and *Kara Bogaz Gol Bay* (1896). Later, in 1922, the work *Kara Bogaz Gol and its Economic Implications* written by Andrusov and Kurnakov was published, in which processes of modern salt accumulation were discussed.

Academician A.P. Pavlov was engaged in research on the stratigraphy of the Jurassic and Cretaceous strata of southern Russia. In addition to a notable advance in paleontology and geotectonics, Pavlov achieved much

success in studying continental deposits; he pioneered in distinguishing two new genetic types of sedimentary deposits, deluvium and proluvium.

Thus, a great amount of information on marine sediments, sedimentary rocks, and ores has been amassed in geology by the late 1920s. The works of geologists of various disciplines set the stage for lithology as a science. Prominent among those who plotted courses in this field were researchers of the academy.

Elected to the academy in the late 19th century were F.B. Shmidt (1885), A.P. Karpinskii (1896), and F.N. Chernyshev (1897); and in the early 20th century, E.S. Fedorov (1901), V.I. Vernadskii (1912), N.S. Kurnakov (1913), N.I. Andrusov (1914), A.P. Pavlov (1916), and A.E. Fersman (1919).

The beginning of the 20th century shook the scientific community of both capitals of Russia. Student riots burst out in Moscow at the end of 1910. They struck Moscow University and were associated with funerals of L.N. Tolstoy. An unjust dismissal of A.A. Manuilov, the rector, and his assistants provoked a unanimous protest of students and lecturers. In January 1911, 207 professors and associate professors of Moscow University headed by academicians K.A. Timiryazev, N.A. Umov, V.I. Vernadskii, S.A. Chaplygin, and P.N. Lebedev sent in their resignations and left the university that substantially weakened the scientific work.

World War I, which started a short time later, adversely affected the Emperor Academy as well; running costs were reduced and some institutions of the academy were closed.

On January 21, 1915, a group of academicians headed by Vernadskii suggested that a regular commission on studying productive forces of Russia should be established within the academy. Its purpose was to study mineral resources, especially those important for military economics: deposits of platinum, salts, radioactive elements, mica, and sapropelites. The commission got funds for publishing an issue *Natural Productive Forces of Russia* and for setting up expeditions. Unfortunately, investigations started by academic geologists were interrupted by revolutionary events in St. Petersburg and Moscow.

III

The postrevolutionary development of lithologic science in Russia was closely related to activities of the Academy of Sciences. Three stages distinguished that time. The first span was the period from the conventional date of the origin of our science (1922) to the lithologic discussion of 1952. The second corresponded to the period from 1952 to 1978. The third stage encloses the 1980s up to the present.

As a consequence of the revolution of 1917, starvation, the following civil war, and emigration of intellectuals, the Academy of Sciences lost many of its members. However, the scientific life did not completely die.

In 1917, the elderly geologist Karpinskii was elected president of the academy at a general meeting. He remained at this post up to the end of 1936. Academician S.F. Oldenburg became an indispensable secretary of the academy. In 1923, the academy comprised 39 members and many corresponding members. They were in charge of 15 institutes, laboratories, museums, and research stations, as well as 21 commissions and editorial boards.

In the 1920s, the Academy of Sciences of the USSR inherited its regulations from the Emperor Academy. The regulations of the Emperor Academy granted several privileges to scientists, making the academy highly independent of the state and the ruling party. For instance, academicians got rights to: (1) nominate and approve (at the general meeting) candidates to members and corresponding members of the academy, taking into consideration only their creative potential and scientific achievements; (2) publish their works without a censorship; (3) use a post service for sending mails free of charge; (4) receive books and journals from abroad without censorship; (5) buy books, journals, devices, and collections abroad and forward them through the customs free of duty; (6) take their works, including manuscripts, off the country without hindrance; (7) be free of customs examination and duty charge when crossing the boundaries of Russia; and (8) use its own heraldic seal.

It is apparent that such regulations could not gain the approval of the state that was striving to control the research work of the country. In 1927, the Council of People's Commissars (CPC) approved new regulations for the academy, according to which its activity was directed "to adapt scientific theories and results of scientific experiments and observations to a practical implementation in industry and the cultural-economic development of the USSR."

The regulations were later reconsidered in 1930, 1935, and 1959 in connection with a considerable expansion of scientific and research work in the academy. The requirements imposed upon scientists to be elected as academicians changed drastically. Clause II in the regulations of 1930 implied that only scientists "contributing much to the construction of socialism in the USSR" can be elected in the academy. Personalities who "showed hostility to the revolutionary movement of the proletariat" should be excluded from nominees. Later, mostly administrators—directors of institutes, officials from ministries and departments—were elected to the Academy of Sciences. Elected honorary members of the academy were the Secretary General of the Central Committee of the USSR Communist Party I.V. Stalin, a Member of the Government V.M. Molotov, and even General Procurator of the USSR A.Ya. Vyshinskii.

According to the CPC's Resolution dated April 3, 1928, the number of the academy members increased to 85; the election of 42 new members was planned and

there were many philosophers-Marxists among proposed candidates. A violent struggle raged around the election of A.M. Deborin, N.M. Lukin, and V.M. Friche. Despite the active opposition of academicians I.P. Pavlov, B.M. Lyapunov, F.Yu. Levinson-Lessing, E.F. Karskii, and others, the vacancies were filled and many functionaries of the communist party joined the ranks of academicians. Similar elections were repeated over and over in succeeding years; in 1929 a communist G.M. Krzhizhanovskii wrote, "We enter the Academy of Sciences as a column of Marxists-dialecticians." The number of academicians in 1930s–1940s increased very fast; it is well known that the number of members of the academy in 1970s was as great as 244, whereas that of corresponding members exceeded 400.

The opposition of "conservative" academicians to the interference of the Communist Party members was suppressed by different measures. The broad public often intervened in academic discussions. In 1928, communists of Leningrad University put the academic opposition on the "right trail" by means of newspapers using such words, "Let the earned obscurants know that the working class going under the banner of the close unity of science with labor will step over them without a moment's hesitation for the sake of that unity. If the present academy will not manage them, we will overstep the academy." Threats were often supported by deeds. For instance, in 1930, an "action" was brought against academician S.F. Platonov, a historian who was arrested along with academicians V.N. Beneshevich, E.V. Tarle, and other scientists, being charged with an attempt to forcibly overthrow the Soviet regime.

At the same time, the life of members of the academy considerably improved. Higher salaries, food allowances, cars and dachas (summer houses) at the public coast, sanatorium and health resort facilities, as well as government awards made the election to the academy tempting and a matter of prestige.

As a consequence, the staff of the Academy of Sciences increased in quantity and changed in quality in the 1930s; many militant philosophers-materialists, such as academicians E.M. Yaroslavskii (M.I. Gubel'man), M.B. Mitin, P.F. Yudin, G.F. Aleksandrov, P.N. Pospelov, appeared in its ranks. Their quest for a leading role in the academy led to a series of ideological discussions in science in the 1940s–1950s.

In 1934, when the Academy of Sciences of the USSR was moved from Leningrad to Moscow, its two divisions comprised 25 institutes, 10 laboratories, 11 commissions, 1 museum, and some experimental stations. The Council on the Study of Natural and Productive Forces operated under the aegis of the general assembly of the academy, whereas the library, archives, publishing house, committee on training of specialists, and two commissions operated under the Presidium. In addition, there were three branches (Urals, Far East, and Transcaucasia) and three research centers.

After the death of Karpinskii, the botanist V.L. Komarov (1936–1945) and later the physicist S.I. Vavilov (1945–1951) were elected presidents of the USSR Academy of Sciences; geological institutes in Moscow were reformed to set up a united academic Institute of Geological Sciences; such "compression" of institutions undoubtedly triggered scientific disagreements.

Immediately after the revolution, scientific works in the Soviet Union republics were gathering force. The National Academy of Sciences of the Ukraine Soviet Socialist Republic was established in 1919; academician V.I. Vernadskii was its first president. In 1928, the Institute of the Belarussian Culture was reorganized into the Academy of Sciences of the Belarussian Soviet Socialist Republic. In areas of former colonial periphery—in the Caucasus, Kazakhstan, and Central Asia—branches and research centers of the Academy of Sciences were set up which gradually changed into republican academies. For instance, the academies of Sciences of the Georgian and Lithuanian Soviet Socialist Republics were established in 1941, and after the Great Patriotic War, the academies of the Azerbaijan (1945), Kazakh (1946), Latvian and Estonian (1946), Tajik and Turkmen (1951), and Kirgiz (1954) republics were set up.

There were hundreds of scientific institutions by the moment of foundation of the Soviet Union (1922). In 1940, the number of research and higher educational institutes reached 2359; 786 belonged to branches and divisions of the USSR Academy of Sciences. By the late 1970s, the total number of institutions was as great as 4985; 2458 of them were branches and divisions of the academy. According to 1970 reports, about 927700 researchers worked in the USSR, among which there were 23600 persons with DSc degrees and 224500 with PhD degrees. As time elapsed, the Presidium of the USSR Academy of Sciences had to take over the function of a coordinator of the research work and turn to the headquarters of science.

The advancement of academic lithology during 1922–1952 depended, to a large measure, on the applied direction of this science. Lithologists focused attention on mineral deposits, some deposits being studied from different standpoints, thus becoming an "apple of discord."

Two slightly competing academic groups showed up in the course of these studies. In the first group were academicians A.D. Arkhangel'skii, I.M. Gubkin, and P.P. Lazarev, who investigated iron ores, bauxite, oil, phosphorites, and other sedimentary mineral deposits. The work was later continued by academician N.M. Strakhov.

The second group comprised works of academicians V.I. Vernadskii, A.E. Fersman, professor Ya.V. Samoilov, who were engaged in the research on iron ores, rare and radioactive elements, sulfur deposits, apatite, and various biogenic rocks (bioliths). Sub-

sequent generalizing works of corresponding member L.V. Pustovalov were in compliance with these schemes.

Lithological works by academician Arkhangel'skii were devoted to the Cretaceous and Tertiary sequences of the Russian Platform and associated mineral deposits. He described facies of ancient water basins in his monograph *Upper Cretaceous Deposits of Eastern European Russia* (1912), as well as defined analogies between modern sediments of seas and oceans, and types of the Cretaceous deposits. Later, Arkhangel'skii published a series of papers and monographs devoted to formation conditions of oil shales (1920–1922), phosphorites (1909–1927; *Phosphorites of the USSR*, 1927), bauxites (1933–1937), oil and gas fields (*Conditions of Oil Formation in Northern Caucasia*, 1927). Prospecting for iron ore got under way under the supervision of academicians Arkhangel'skii, Gubkin, and Lazarev in the Kursk magnetic anomaly area during the civil war. The work continued until the late 1930s and resulted in revealing the richest deposits of ferruginous quartzites (a series of papers, 1924–1926).

The genesis of oil shales and formation conditions of oil and gas pools were studied in detail by Gubkin; he issued the monograph *The Study of Oil* (1932, 1937) and a great number of works confirming perspectives of the prospecting for oil pools in the Russian Platform, Cis-Ural, Crimea and Caucasus.

In the monograph *Geologic Structure and History of the Black Sea* (1938), Arkhangel'skii and Strakhov described in detail the types of modern and ancient bottom sediments and their stratigraphy, studied the mechanism of precipitation, and showed the relationship between sedimentation and the topography of drainage areas. Sediments were studied by the methods similar to those used for ancient sedimentary rocks; this later allowed Arkhangel'skii to apply the obtained data for reconstructing formation conditions of Tertiary oil-bearing sequences in Dagestan. Thus, the studies of such trend pioneered in the 1920s–1930s were of great methodological importance and opened the way to a wide use of the comparative–lithologic method in future.

Pursuing this work, Strakhov studied the formation of conditions oil shales in the Cis-Ural region and Russian Platform (*Oil Shales of the Perisphinctes Pandori d'Orb Zone*, 1934; *The Domanik Facies of Southern Ural*, 1939, and others), as well as climatic conditions and structural environment for location of hypogene iron ores (a series of papers, 1940). His monograph *Iron Ore Facies and Their Analogs in the Earth's History* (1947), awarded with the State Prize of the USSR, was published after the Great Patriotic War. The book sums up the studies of iron and manganese ores as well as bauxite. Strakhov's two-volume monograph *Historical Geology*, which reviews paleogeographic materials of the world, was published in 1937–1938.

During 1922–1951, sedimentary rocks and ores became subjects of the mineralogical–geochemical analysis as well. Vernadskii, Fersman, and their disciples examined in their works isomorphism and paragenesis of elements and minerals, Clarke values or the average content of elements in the crust and sedimentary rocks, ore concentrations, mineral deposits, belts, provinces, different spheres of the Earth, and their interaction. Attempts were made to trace the history of elements in different processes of rock and ore formation; the role of natural radioactivity and living substances in geological phenomena were defined. The problems mentioned above were treated in monographs by Vernadskii *Outlines of Geochemistry* (1924), *Biosphere* (1926), and *History of Minerals in the Earth's Crust* (1927), as well as in a multi-volume book by Fersman *Geochemistry* (1933–1934); many sections of the works essentially represent the commentary of the sedimentary process from the viewpoints of a chemist and mineralogist.

The mineralogical and geochemical study of iron ores from Tula and Lipetsk deposits of the Russian Platform, as well as the Black, Baltic and Barents seas, was carried out by Vernadskii's disciple, professor Samoilov (a series of papers, 1900–1917). He headed the Commission on phosphorites and studied in detail the mineralogical–geochemical composition of major phosphate deposits in the world (a series of papers, 1908–1925), as well as celestine and barite deposits (a series of papers, 1908–1912).

After the revolution, Fersman organized a number of expeditions to the central part of the Kola Peninsula which resulted in the discovery of new minerals and the development of the richest apatite–nepheline deposits (a series of papers, 1920–1929). He later visited and extensively investigated Sernye Bugry (Turkmenistan), radium ore manifestations in Fergana (Uzbekistan), and crossed Kara Kum together with academician D.I. Shcherbakov.

Corresponding member of the academy L.V. Pustovalov, a disciple of Samoilov and Fersman, continued the studies of Samoilov. He carried out an extensive study of the Jurassic iron ores from the Tula and Lipetsk deposits and developed the "lacustrine-boggy" hypothesis for their genesis (*The Genesis of Lipetsk and Tula Iron Ores*, 1933). Later, he tried to identify a general scheme of sedimentary rock and ore formation; his three-volume monograph *Petrography of Sedimentary Rocks* was published in 1940. The author proposed to consider the sedimentation process as a result of the mechanical and chemical differentiation of a substance, as well as substantiated the physiochemical mechanism of the phenomenon, minimizing the importance of biologic factors. He also pointed out that periodicity of the tectonic life on Earth was reflected in a regular recurrence of some rocks and ores through time.

Pustovalov believed that geochemical environments, which were prevailing on the bottom of paleoba-

sins during sedimentation, retained in the course of secondary rearrangements (the law of physiochemical succession) and, thus, the sedimentation stage was undoubtedly a decisive stage of the sedimentary process.

In a separate chapter of the book, he sharply criticized the comparative–lithologic method proposed by Arkhangel'skii and Strakhov, and suggested that actualistic reconstructions should be viewed with great caution. As a whole, the idea of sedimentary differentiation allowed Pustovalov to arrange the lithologic–petrographic descriptions of different types of sedimentary deposits into a definite series and to impart a certain harmony to the pile of formerly disordered facts.

Despite the overall likelihood and persuasiveness, the system built up by Pustovalov was not entirely consistent with the facts known at that time. It became obvious since 1940 that disagreements between Pustovalov and Strakhov were deep enough and could be solved only in the course of common discussion of lithologists. However, the Great Patriotic War interrupted the normal course of scientific life in the country, and discussion of the controversies was postponed for a while.

To sum up this section, I would like to point out that the works mentioned here do not exhaust the achievements of lithologists, geochemists, and mineralogists of the USSR Academy of Sciences during the period of 1922–1952. Left aside are remarkable monographs by academicians N.S. Kurnakov (*Solar Evaporation of Sea Water and Salt Brines of Lakes*, 1938), P.I. Stepanov (*The Theory of Belts and Groups of Coal Accumulation*, 1947), Yu.A. Zhemchuzhnikov (*General Geology of Caustobioliths*, 1935; *Seasonal Varying and Periodicity of Sedimentation*, 1962), D.V. Nalivkin (*Principles of Facies*, 1933), A.N. Zavaritskii (*Introduction to Petrography of Sedimentary Rocks*, 1932), N.S. Shatskii (*Geological Structure of the Eastern Part of Black Mountains and the Miatly and Dylm Oil Fields*, 1929), B.B. Polynov (*Weathering Crust*, 1934), and others. A more complete list of them is given in *Evolution of the Lithology in the USSR and Its Immediate Tasks* (*Litol. Polezn. Iskop.*, 1967, no. 5).

IV

The lithologic discussion was held on November 17–24, 1952 at the 1st Conference on Sedimentary Rocks and Mineral Resources which was organized in Moscow on the initiative of the Division of Geologic–Geographic Sciences, the USSR Academy of Sciences. Twenty individual and collective reports of lithologists, tectonists, and stratigraphers were presented, but the lectures given by Pustovalov, the Chairman of the Organizing Committee, on *The Strategy of Study and Basic Purposes of Investigating Sedimentary Rocks and Mineral Deposits* and Strakhov on *The Problem of Distribution and Accumulation of Major Chemical*

Components in Sediments of Modern and Ancient Water Basins undoubtedly represented the key reports. The conference was attended by 1077 specialists representing 195 research and geoprospecting institutions as well as higher educational institutes. Sixty-seven scientists took part in the discussion.

An address delivered by the Organizing Committee copied the polemical methods of ideological discussions held previously in the Academy of Sciences in the field of mathematics, physics, and especially biology; also presented here are scientific arguments whimsically interlaced with citations from the classics of Marxism-Leninism and the calls to strengthen the applied science. The presentation made by Strakhov was constructed more rigorously, discussing purely scientific problems.

In contrast to the notorious biologic session of the Lenin All-Union Academy of Agriculture (VASKhNIL) (August, 1948), the first lithologic conference did not provoke sharp organizational conclusions; moreover, it provided the background for extending the lithologic studies in Russia.

Summing up the discussion, the conference on sedimentary rocks resolved: (1) to consider "the manner of solving the genetic problems by comparative correlation of heterochronous rocks (relative to each other) and ancient rocks relative to modern sediments. This approach was named in the Soviet science the comparative-lithologic method, as being rightful and in some cases fruitful..." (*Decision...*, 1983, p. 11); (2) to point out that "the scheme of sedimentary differentiation... does not show changes in the course of sedimentary differentiation in the geologic history of the Earth and under different climatic conditions and structural environment, as well as does not take into account a peculiar role of organisms during sedimentation" (*Ibidem*, p. 12).

Based on the conference decisions, the Commission on Sedimentary Rocks was established under the Division of Geology and Geophysics, the USSR Academy of Sciences. The commission represented a special research center for coordination of scientific work in the field of studying the sedimentary rocks and ores. It was headed by the corresponding member of the USSR Academy of Sciences N.M. Strakhov and V.S. Yablokov, PhD (Geol.-Miner.). Later, in the 1970s, when the Commission was headed by academician A.V. Sidorenko, it was reorganized into the Interdepartmental Lithologic Committee (ILC). Corresponding member of the USSR Academy of Sciences P.P. Timofeev was elected chairman of the ILC in 1978. During the period from 1952 to 1984, the ILC held 12 all-union conferences, a plethora of seminars, and meetings of bureaus and sections.

Of particular importance among the lithologic conferences were: the 2nd All-Union Conference held in Lvov (1955) was devoted to mineralogy and geochemistry of sedimentary rocks; the 4th All-Union Confer-

ence (Tashkent, 1959) discussed the problems of formational and facies analyses in the context of prognosticating the occurrence of sedimentary mineral deposits; the 5th All-Union Conference (Novosibirsk, 1961) was dedicated to the methods of compilation of lithofacies and paleogeographic maps, as well as to problems of formation of mineral deposits related to weathering crusts; the 6th All-Union Conference (Tbilisi, 1963) was devoted to the analysis of volcanosedimentary, rock- and ore-formation; the 7th All-Union Conference held in Moscow (1968) was concerned with geochemistry of sedimentary rocks and ores; the 10th All-Union Conference (Petrozavodsk, 1973) discussed the Precambrian lithology and sedimentary geology; and the 11th All-Union Conference (Moscow, 1979) under the motto "Lithology at a new stage of developing geological knowledge" was devoted to the most important theoretical problems of lithology. Using the materials of these undertakings, the Commission on Sedimentary Rocks and the ILC published a variety of collected articles on lithology.

The journal *Litologiya i Poleznye Iskopaemye*, established in 1963, was designed to elucidate scientific advances in the field of studying modern sediments as well as ancient sedimentary rocks and associated mineral deposits. N.M. Strakhov was elected member of the academy in 1953 and became the editor-in-chief, with V.S. Yablokov as deputy editor-in-chief. Later, G.I. Bushinskii, DSc (Geol.-Miner.) was nominated editor-in-chief (1969-1981) with V.N. Kholodov as deputy editor-in-chief. In 1981, after Bushinskii had passed away, Kholodov was elected editor-in-chief. The history and activity of the journal were discussed in more detail in the paper by Kholodov *The 35 Anniversary of the Journal Litologiya i Poleznye Iskopaemye* (1998, no. 4).

Pustovalov was elected corresponding member of the USSR Academy of Sciences in 1953; in 1961, he established the Laboratory of Sedimentary Mineral Deposits, the first research center in the USSR aimed at studying mineral deposits of the sedimentary origin. In compliance with resolutions of the 1st All-Union Conference on Sedimentary Rocks, the Department of Lithology and Marine Geology was set up in the 1980s in Moscow State University under the aegis of P.P. Timofeev, corresponding member of the USSR Academy of Sciences.

The period from 1952 to 1978 in the academy was the time of presidency of A.N. Nesmeyanov (1951-1961), M.V. Keldysh (1962-1975), and A.P. Aleksandrov (1975-1986). It was the time of the most important scientific generalizations in the lithology under the supervision of academician Strakhov. During this stage, Strakhov and his colleagues prepared and published monographs *Calcareous-Dolomitic Facies of Modern and Ancient Water Basins* (1951), *Formation of Sediments in Modern Water Basins* (1954), *Types of Dolomite Rocks and Their Origin* (1956) a two-volume

book *Methods of Studying Sedimentary Rocks* (1957), *Geochemistry and Lithology of Paleozoic Sedimentary Rocks* (1955), *Outlines of the Geochemistry of Upper Paleozoic Deposits of the Humid Type* (1959), *Geochemistry of the Sedimentary Manganese Ore Process* (1968), *Elaboration of Lithologic Ideas in Russia and the USSR* (1971), *Problems of Geochemistry of the Modern Oceanic Lithogenesis* (1976), and *Geochemistry of Modern Sedimentogenesis* (1979). Besides, in a series of papers published in various journals, Strakhov discussed problems of diagenesis and other stages of sedimentary rock formation, mechanisms and implications of volcanic processes, the genesis and classification of different mineral resources; he published several fundamental works and took an active part in all-union conferences, seminars, and colloquia.

The documentary material accumulated mainly in the post-war period, as well as particular theoretical works, were generalized by Strakhov in his monographs *Fundamentals of the Theory of Lithogenesis* (1960–1962) and *Lithogenesis Types and Their Evolution in the Earth's History* (1963). The books should undoubtedly be considered as the peak of the scientific work of Strakhov. A three-volume monograph by Strakhov was rewarded with the Lenin Prize; the three volumes were later translated into English in the USA. In 1967, Strakhov was awarded the Karpinskii Gold Medal by the presidium of the USSR Academy of Sciences for the manual *Lithogenesis Types and Their Evolution in the Earth's History*; the work was translated into Japanese. The works by Strakhov methodologically leant upon the comparative-lithologic method and the systems analysis.

Over several decades, Strakhov extensively studied the types of modern sediments of lakes, seas, and oceans, searched for their old homologs, and synthesized data on the mechanism of their formation. He paid much attention to the geochemical characteristics of fossils. The chemical analysis allowed the introduction of quantitative parameters into models, as well as a comparison with the mathematical accuracy.

It is interesting to note that Strakhov's theoretic schemes intuitively contained all the features of the systems analysis. He always knew how to consider the process of sedimentary rock formation at the level of a chemical element, mineral, rock, facies, formation, and lithosphere as a whole; geochemistry was a principal instrument of such a comprehensive approach.

Strakhov wrote in one of his program papers: "The introduction of chemistry in the modern lithology is undoubtedly a progressive phenomenon as it extends the bounds of knowledge of the composition of sedimentary rocks and ores, introduces a number and a measure into our knowledge, makes it more objective and precise, thus bridging the gap between the science of sedimentary rocks and the group of exact sciences. The descriptive works, which dominated in our science until recent times and are popular even now, give way

gradually to genetic works, the studies of matter transformation process, i.e. the geochemical processes. A new branch of geology—geochemistry of sedimentary rocks and ores—is being conceived now in the midst of lithology; the aim of the branch is to cognize the history of all elements involved in the formation of sediments, rocks, and ores" (Strakhov, 1968, p. 3).¹ Academician Strakhov was recognized as the founder of the geochemistry sedimentary process.

A large body of lithologic research of various trend was carried out by members of the academy during the period from 1951 to 1978. Here, we should mention the works by academician A.P. Vinogradov *Geochemistry of Rare and Trace Elements in Soils* (1957), *Chemical Evolution of the Earth* (1959), *Introduction to Ocean Geochemistry* (1967); by academician A.B. Ronov *Sedimentary Sphere of the Earth* (1980); a two-volume work by D.V. Nalivkin *Study of Facies* (1956); works by academician F.V. Chukhrov *Colloids in the Earth's Crust* (1955); and by academician V.I. Vernadskii *Chemical Structure of the Earth's Biosphere and its Surroundings* (1965). Academician A.V. Sidorenko in his monographs *The Lithologic Study of Metamorphic Strata* (1961) and *Organic Matter in the Precambrian Sedimentary-Metamorphic Strata* (1974) substantiated a new methodological approach to the study of highly-altered Precambrian strata, argued about the carbon dioxide and hydrocarbon breathing of the Earth, and, following Vernadskii, noted the extreme antiquity of the organic matter.

Academician B.S. Sokolov covered general problems of the evolution of the Precambrian biosphere in a series of works (1976–1995). Some works by academician N.S. Shatskii (1955–1965) laid the foundation of the formation analysis and covered the problems of genesis of phosphorus- and manganese-bearing formations. The works by academician A.P. Lisitsyn *Sedimentogenesis in Oceans* (1974), *Processes of Oceanic Sedimentation* (1978), *Avalanche Sedimentation and Hiatuses in Seas and Oceans* (1988), and others were of great importance for the development of the lithology of modern sediments.

Papers by Yu.A. Zhemchuzhnikov (1952–1955), corresponding member of the USSR Academy of Sciences, and especially his monograph *Fundamentals of the Coal Petrology* (1960) contributed much to the advancement of coal geology and the study of facies. P.P. Timofeev, corresponding member of the USSR Academy of Sciences, who continued these works, was rewarded the State Prize of the USSR for the two-volume monograph *Geology and Facies of the Jurassic Coal-Bearing Formation of Southern Siberia* (1969) and *The Jurassic Coal-Bearing Formation of Southern Siberia and Depositional Conditions* (1970). Corresponding member of the USSR Academy of Sciences N.B. Vassoevich and his follower, corresponding mem-

¹ *Geokhimiya osadochnykh porod i rud* (Geochemistry of Sedimentary Rocks and Ores), Moscow: Nauka, 1968. Foreword.

ber B.S. Sokolov substantiated the lateral-migration theory of formation of oil and gas fields in a series of works (1961–1986).

Works by academician A.L. Yanshin were of great importance. He elucidated the problems of evolution of geological processes in the Earth's history (collected articles *Evolution of Geological Processes*, 1989; the monograph *Evolution of Geological Processes in the Earth's History*, 1988; *History of the Atmosphere*, 1985, and others). A.L. Yanshin and M.A. Zharkov studied comprehensively the processes of phosphorization and salt deposit accumulation (*Phosphorus and Potassium in Nature*, 1986).

The USSR Academy of Sciences devoted a large body of research to sedimentary mineral deposits. The monograph by academician A.G. Betekhtin *Commercial Manganese Ores in the USSR* (1956) is of particular interest among the works published on this topic, as well as is the monograph by academician N.A. Shilo *Fundamentals of Placer Deposits* (1985), the handbook by academician V.I. Smirnov *Geology of Mineral Deposits* (1969, 1976), the monograph by academician N.P. Laverov *et al. Evolution of Uranium Ore Formation in the Earth's History* (1979), collective three-volume work *Geochemistry, Mineralogy, and Genetic Types of Rare Metal Deposits* (1966) edited by K.A. Vlasov, corresponding member of the USSR Academy of Sciences, which was rewarded the State Prize of the USSR.

V

The recent stage in the lithologic history occupies the period from 1978. Academician Strakhov passed away on July 13, 1978. The "golden age" of Russian geology is closely associated with the name of this prominent scientist.

Within the period of the 1980s–1990s, the academy was headed by presidents A.P. Aleksandrov (1975–1986), G.I. Marchuk (1986–1991), and Yu.S. Osipov (1991 to the present).

At that time, our country was shaken by many political events. The Chernobyl tragedy, political riots in the 1980s, the collapse of the Soviet Union, the loss of a unified geologic space in the 1990s, and finally the Chechen war, as well as economic and political crises, which burst out in Russia, depressed the financing and general progress in science of the Russian Academy of Sciences (RAS).

Meanwhile, the tendency in the development of lithology changed greatly; some academic institutes (Geological Institute, Shirshov Institute of Oceanography, and others) reduced laborious and expensive studies of the composition of sedimentary rocks and ores which involved geochemistry and mineralogy.

Although the Geological Institute is continuing geochemical studies of manganese, ferromanganese, phosphate, and black shale sedimentary and hydrother-

mal-sedimentary deposits (scientific school of academician Strakhov, key researcher—V.N. Kholodov), the petrographic and textural studies of sediments and sedimentary rocks increasingly receives attention in theoretical investigations of most lithologic institutions in Russia; more emphasis is placed on formal petrographic classifications of sedimentary deposits, on the use of the texture analysis, and the combination of purely petrographic features being presented as a combined genetic approach.

There are suggestions to give much thought to the facies analysis, though the facies themselves are mostly studied at the rock level only by petrographic and sometimes visual methods. Small-scale geologic subjects, such as geological formations and sedimentary basins, attract particular interest in relation to the development of geotectonics; however, the lithologic approach often appears to be formalized. It is observed well because the real application of the formation analysis in modern lithology is restricted only to speculations concerning the definition of the term "formation", whereas the study of sedimentary basins is not methodically different from the ordinary paleogeographic analysis.

I believe the main object of modern Russian lithology consists in the turning back of the methodology and methods elaborated by N.M. Strakhov.

First of all, it is necessary to continue the study of chemistry of ancient lithologic objects and to closely link geochemistry with mineralogy of sedimentary deposits. Special studies characterizing the composition of facies, formations, and related mineral deposits should be set up. In the long run, moving towards the suprarock level of studies, the problem can then be raised on the true geochemistry and mineralogy of sedimentary basins and on the composition of the lithosphere as a whole. For example, the original material and calculations made earlier by academician A.B. Ronov require, in some cases, more concrete definitions and refinements. Besides, one should bear in mind that, at present, a researcher-geochemist can considerably extend the range of the studied chemical elements by introducing the rare, minor, radioactive elements, and even such elements as platinoids, polonium, actinides, and other rarities.

The geochemical-mineralogical study of modern sediments is extremely interesting. The study is carried on to one extent or another in various academic institutions (for instance, in the Geological Institute, Institute of Oceanography, Institute of the Lithosphere, etc.); however, the successive use of the comparative-lithologic method requires refinement of many data and determinations made earlier. In addition to the improvement of our knowledge of the composition of sedimentary rocks, the lithology should handle a variety of traditional problems.

One of such problems is associated with the study of deposits making up the sedimentary cover of modern

oceans and seas. Deep-sea drilling within the oceanic sequence provides the lithofacial characteristics of the Mesozoic–Cenozoic deposits, general scenario of the ocean evolution, and geochemical balance of the oceanic substance. Thus, it allows us to appreciate the role and significance of volcanic phenomena in the oceanic sedimentation, to reconstruct formation conditions of associated mineral deposits, and to pose the question about the possibility of their commercial use.

Another problem in lithology is the further development of the Precambrian theme. The reconstruction of sedimentation conditions in the Precambrian requires, on one hand, a cognition of the essence of the catagenetic and metamorphic transformations, and on the other hand, allows us to reconstruct a tremendous time span in the Earth's geologic history, which is seven times greater than the apparent history of the Phanerozoic. The study of the processes of metamorphism and especially ultrametamorphism is, in turn, a key to understanding the endogenic processes as a whole and the genesis of some endogenic mineral deposits in particular. Besides, the major sedimentary mineral deposits are related to the Precambrian. Among these, there are deposits of iron ores, sulfides, platinum, diamonds, and gold placers, which impart an important practical aspect to the problem of studying the oldest deposits.

One should point out the necessity of further study of formation conditions and regularities in distribution of various sedimentary mineral deposits ranging from iron ores, bauxites, coals, phosphorites to accumula-

tions of rare, disseminated and radioactive metals. Not only isolated mineral deposits should be studied but entire metallogenic provinces as well, and genetic relationships between different groups of mineral deposits should be considered within such ore provinces.

Particular emphasis should be placed on mineral deposits of the volcanosedimentary and exhalative–sedimentary genesis. Unbiased criteria should be elaborated in this field which distinguish the endogenic and epigenetic material from sedimentary or syngenetic. Another intriguing problem deals with the study of the ore-forming role of epigenetic processes and the elaboration of methods for investigating various epigenetic deposits of rare, base, and radioactive metals.

Significant and independent problems are provided by the geochemistry of sedimentary and volcanosedimentary ores, which become very urgent in recent years due to the necessity of their quantitative assessment, as well as experimental lithology, paleogeography, paleohydrogeology, geochemistry of oil and rock asphalt, and other fast developing branches of our science.

The Academy of Sciences played a significant part in posing all these problems. Hopefully, the academic institutions of our country will occupy a prominent place and supervise the research work in solving the problems, thus, assisting the Russian economy with raw materials.

Postglacial Sedimentation History in Shelf Depressions of the Barents Sea

I. O. Murdmaa and E. V. Ivanova

Shirshov Institute of Oceanology, Russian Academy of Sciences, Nakhimovskii pr. 36, Moscow, 117218 Russia

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Abstract—Based on the study of 30 cores of bottom sediments obtained from the shelf depressions in the central, northern, and eastern parts of the Barents Sea during cruises 11 and 14 of the R/V *Akademik Sergei Vavilov* (1997–1998), three main stages of postglacial sedimentation, corresponding to the Holocene, late and early deglaciation stages, are discussed. The early deglaciation stage was marked by accumulation of relatively coarse glaciomarine sediments (sandy-silty-clayey material with gravel and pebble). The late deglaciation stage was characterized by the bottom sediment transport and reworking with formation of laminated sediments of nepheloid flows and turbidites. This process was accompanied by a high influx of the fine terrigenous material transported by thawed waters of retreating glaciers. Based on the lithological and micropaleontological (foraminifers) data, several stages reflecting changes in the intensity of the influx of Atlantic water to the Barents Sea are defined in the Holocene history of usually normal marine sedimentation.

The Barents Sea is one of the key areas for deciphering the postglacial evolution of climate and World Ocean water circulation. This area is the most distant one, where warm water penetrating from the North Atlantic intermixes with the cold Arctic water. Our study was aimed at the reconstruction of paleoceanographic and paleoclimatic environments in the Barents Sea in connection with changes of the global climate and water circulation in the World Ocean after the last glacial maximum (LGM). This time period corresponds to the period of breakdown of continental ice shields in the northern hemisphere (deglaciation) and development of the Holocene paleoceanographic situation close to the modern environment.

This work considers the preliminary results of the study of the history of postglacial sedimentation recorded in bottom sediment sequences that were recovered by gravity corers from some shelf depressions in the central, northern, and eastern parts of the Barents Sea. The sufficiently high thickness of postglacial sediments in some depressions allows the evolution of sedimentation processes reflecting short-term paleoclimatic and paleoceanographic events to be studied in detail.

Recent and Upper Quaternary sediments of the Barents Sea were considered in many publications beginning from classic works by Klenova (1960) to works published during the last decade (Gataullin *et al.*, 1993; Gurevich, 1995; Murdmaa *et al.*, 1998a, 1998b, 1998c; Pavlidis, 1992; Pavlidis *et al.*, 1998; Polyak *et al.*, 1995, 1997; Samoilovich *et al.*, 1993; Tarasov, 1998; and many others). Several sedimentary sections obtained from the western, northern, and eastern peripheral areas of the basin were dated using the mass-spectrometer radiocarbon method (Elverhøi and Sol-

heim, 1983; Gataullin *et al.*, 1993; Hald *et al.*, 1999; Knies *et al.*, 1999; Lubinski *et al.*, 1996; Polyak and Solheim, 1994; Polyak *et al.*, 1995, 1997). The listed works contain lithological descriptions of sediments, data on proportions of microfossils and their oxygen and carbon isotopic composition. The obtained data that used these and some other new methods led to the revision of some previous concepts on the history of postglacial sedimentation that were formulated as a result of marine geological investigations carried out by Russian researchers during many years.

The Recent geological history of the Barents Sea remains debatable. Presently, there are two competing points of view on the paleogeographic situation of the Barents Sea shelf during the LGM. According to the first view, the shelf was covered by a continuous thick ice shield, which rested upon the ground and whose edges reached the upper part of the continental slope, at least to the depth of 500 m (see for instance, Grossval'd, 1983; Polyak and Mikhailov, 1996; Polyak *et al.*, 1995). Other authors (for instance, Matishov, 1984; Pavlidis *et al.*, 1998) assume that the existence of several ice shields resting upon archipelagoes and some shoals, between which small sea basins covered by pack ice and shelf glaciers, were located at the place of modern shelf depressions.

Accordingly, sedimentation processes and paleoceanographic conditions during the deglaciation period are interpreted in different ways. The Holocene stage of evolution is generally considered by most authors as a period of the formation of the paleoceanographic situation close to the modern one. Nonetheless, the evolution of sedimentation processes during this stage requires further study, particularly in connection with the recent intense development of high-resolution

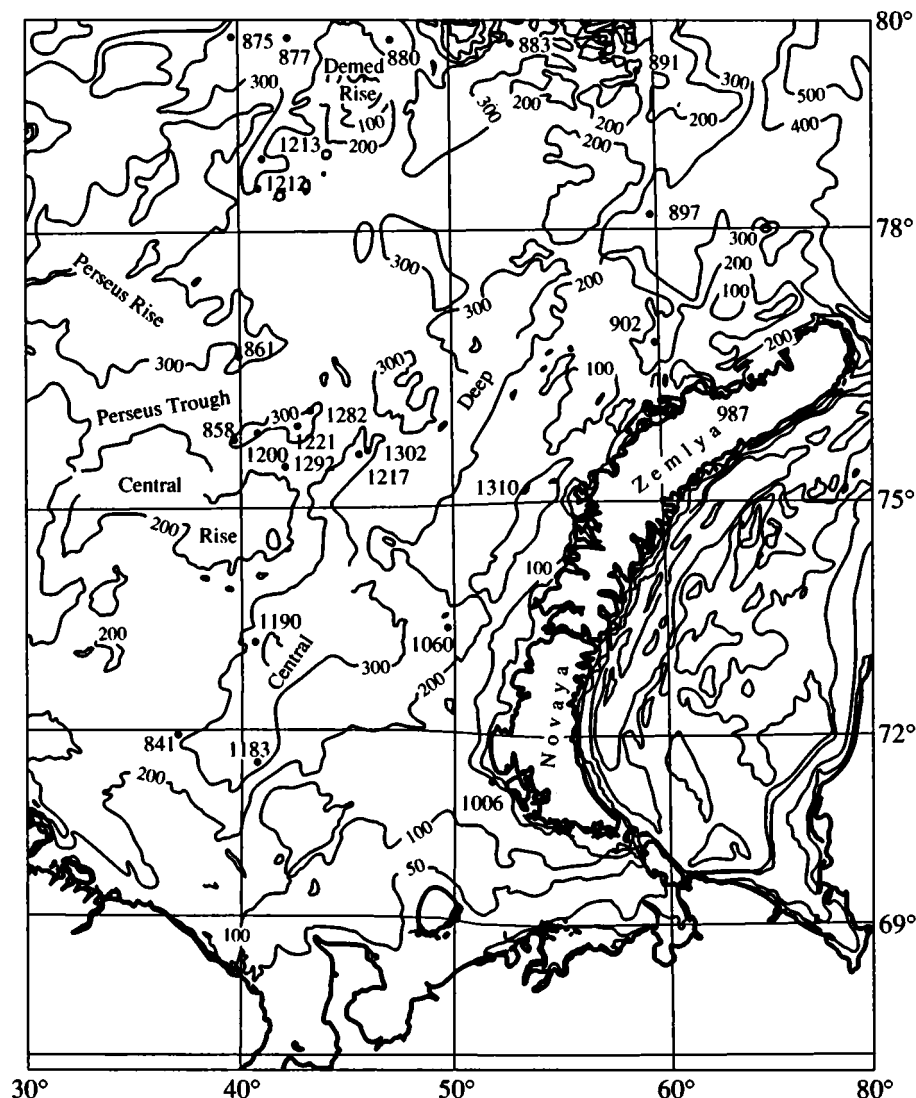


Fig. 1. Location of sampling sites in cruises 11 and 14 of the R/V *Akademik Sergei Vavilov*.

paleoceanography and paleoclimatology of the last climatic cycle (the last 125 ka).

In cruises 11 and 14 of the R/V *Akademik Sergei Vavilov* (1997–1998), 30 cores of bottom sediments were obtained from the shelf depressions with elevated sedimentation rates, including those in the least studied central areas of the Barents Sea. The work discusses preliminary results of the thorough lithological and micropaleontological study of these cores.

MATERIALS AND METHODS

In this study, cores of bottom sediments were sampled in cruises 11 (1997) and 14 (1998) of the R/V *Akademik Sergei Vavilov* along submeridional profiles at 40° E and 41° E in depressions with elevated thickness of the postglacial sedimentary cover (Gurevich, 1995): in troughs south of the Franz Josef Land, in the Central

Deep, and in the West Novaya Zemlya Trough (Fig. 1). Gravity corers with external diameters of 165 and 127 mm were used in cruises 11 and 14, respectively. In total, 30 cores (1.26 to 5.96 m long) were obtained in two cruises from the depth interval of 171 to 457 m (table). Sampling sites were selected after considering records of continuous high-frequency (3–4 kHz) seismic profiling performed under the supervision of L.R. Merklin (Cruise 11) and A.F. Byakov (Cruise 14) using the seismoacoustic profile recorder "Parasound" with the resolution of about 0.5 m (along the section) at these depths. This allowed sampling sites to be tied to bottom topography and structures of the postglacial sedimentary cover. In order to perform lithostratigraphic interpretation, sampled core sections were correlated with seismic records obtained at sites during the ship drift.

A detailed lithological description, preliminary study of smear-slides, and express analysis of foramin-

Main characteristics of sediment cores from the Barents Sea obtained in cruises 11 and 14 of the R/V *Akademik Sergei Vavilov*

Station	Coordinates		Water depth, m	Core length, m	Thickness of horizons, m		
	N	E			I	II	III
841	77°56.6'	37°03.6'	290	1.26	0.30	0.40	0.56
858	75°50.6'	39°54.8'	312	3.56	2.07	0.49	1.00
861	76°43.0'	40°05.2'	196	2.94	0.86	0.44	1.64
875	79°56.6'	39°48.4'	315	4.56	0.35	0.41	3.80
877	79°55.0'	42°29.7'	358	4.20	0.10	0.30	3.80
880	79°55.5'	47°08.2'	388	5.08	3.10	0.94	0.90*
883	79°49.9'	53°01.4'	457	4.17	2.55	0.60	1.02
891	79°29.3'	59°06.3'	315	4.63	2.28	1.30	1.05
897	78°06.0'	59°56.2'	365	2.31	0.72	0.14	1.45
902	76°51.0'	59°58.6'	268	3.85	2.90	0.24	0.71
987	76°12.2'	62°29.1'	171	5.96	5.96	—	—
1006-1	71°07.4'	52°00.9'	182	4.45	4.45	—	—
1006-2	71°07.8'	52°02.1'	179	5.83	5.83	—	—
1060	78°21.9'	49°50.4'	252	2.95	1.50	0.34	1.11
1183	71°28.3'	40°48.3'	330	4.17	2.63	1.54	—
1190	73°12.4'	40°56.4'	316	2.76	0.23	=	2.53
1200-1	75°54.4'	41°00.5'	308	3.60	2.25	0.47	1.88
1200-2	75°54.3'	40°59.1'	312	3.33	2.00	0.33	1.00
1212	78°30.6'	40°57.1'	289	2.04	0.12	0.48	1.44
1213	78°39.1'	41°04.0'	326	2.50	1.12	0.59	0.79
1217-1	75°39.5'	45°39.5'	313	2.20	0.52	0.13	1.55
1217-2	75°37.6'	45°42.6'	313	2.12	1.03	0.27	1.09
1221	75°59.8'	32°47.9'	357	3.75	3.26	0.03	0.49
1282-1	76°11.1'	43°29.9'	330	1.77	0.40	0.10	0.27
1282-2	76°11.2'	43°28.5'	328	2.22	0.46	0.24	1.52
1283-2	75°33.7'	43°09.9'	341	1.77	1.77	—	—
1283-3	75°34.8'	43°09.1'	328	2.24	2.07	0.17	—
1302	75°39.5'	46°09.7'	306	2.70	0.78	0.39	1.53
1310-1	75°06.3'	53°26.7'	228	3.89	2.95	0.94	—
1310-2	75°06.1'	53°21.7'	228	4.20	3.89	0.31	—

Note: Below horizon III (in hole bottom), similar pebbly loam was recovered (4.94–5.08 m); for all other cores, the apparent thickness is shown; (—) horizon is not penetrated; (=) horizon is missing.

ifers in the > 0.1-mm fraction of samples taken with the 10–50-cm step were carried out on board. Based on these studies, preliminary subdivision of the sediment sections was performed, and cores with high sedimentation rates and abundant microfossil assemblages sufficient for the detailed study were defined. Presently, two cores taken from the eastern branch of the Franz Victoria Trough (ASV-880) and from the Perseus Trough (ASV-858) are most thoroughly being studied.

Samples (1–2 cm) for the analysis collected from 6 cores with the step of 5 cm were washed through sieves by distilled water to obtain coarse fractions

(0.05–0.1 mm and coarser) for further isotope and micropaleontological studies and for radiocarbon dating of sediments. The weight of natural sediment in every sample varied from 100 to 500 g. Samples and fractions to be analyzed were weighed, and the obtained values were then used for the calculation of weight percents of coarse fractions.

The > 0.1 mm fraction was used for the foraminiferal analysis. In one-fourth part of every sample, 200–300 benthic foraminifer specimens were counted, and the content of planktonic foraminifer shells was calculated.

The complete granulometric composition of samples was determined in some samples using the combined method of V.P. Petelin (analysts V.P. Kazakova and A.N. Rudakova). The organic carbon and calcium carbonate contents were determined by A. Gordeev using the carbon analyzer AN-7529. The chlorine ion content in interstitial water was determined using the titration method by G.A. Pavlova on board, and the results were interpreted by Yu.A. Bogdanov and N.V. Pimenov (Murdmaa *et al.*, 1997).

MODERN SEDIMENTATION ENVIRONMENTS

The Barents Sea shelf is characterized by the strongly differentiated topography (Fig. 1). The spacious Central Deep with depths ranging from 200 to 350 m is located in the study area east of 40° E and north of coastal shoals. It represents a topographic reflection of the Late Paleozoic Barents Sea rift, where modern paleoceanographic investigations were virtually not carried out until recently. Several cores were obtained from this largest shelf depression: ASV-841, ASV-1183, and ASV-1190 from the Central Deep proper and ASV-1200–ASV-1302 in the area of its conjunction with the Perseus Trough. In the west, the deep is bounded by the large isolated underwater Central and Perseus rises divided by the narrow Perseus Trough up to 350 m deep; Cores ASV-858, ASV-861, and ASV-1200 were obtained in the latter (Fig. 1).

In the northwestern continuation of the rift graben, between the Spitsbergen Archipelago and Franz Josef Land, the shelf edge is cut by the Franz Victoria Trough with a complex structure and depth up to 380 m at the latitude of 80° N (where latitudinal profile ASV-11 passes). The trough opens northward to the continental slope of the Arctic Ocean and has a form of a canyon with a deep-sea fan registered by seismic studies near its mouth (Lubinskii *et al.*, 1996; Polyak and Solheim, 1994). To the south, the trough branches into two *sleeves* divided by the Demed Bank in the area between 76° and 80° N. Cores ASV-875, ASV-877, and ASV-1213 are taken in the western part of the trough, and Core ASV-880 is taken in its eastern part (the Demed Trough).

In the north, the Central Deep is bounded by sublatitudinal rises, which are cut by deep troughs (to 500 m deep) near the Franz Josef Land; in one deep trough, Core ASV-883 is taken from the depth of 457 m. In the northeast, the wide pass between the Franz Josef Land and Novaya Zemlya represents the wall of the large Saint Anna Trough, in the sublatitudinal branch of which (the Sedov Trough) Core ASV-897 was taken from (Fig. 1, table).

The eastern wall of the Central Deep is formed by slopes of several swell-shaped rises (the Admiralteiskii Swell) separated from the Novaya Zemlya by the Western Novaya Zemlya Trough, where Cores ASV-902, ASV-1310, ASV-1006, and ASV-1060 were obtained

(Fig. 1). Core ASV-987 is sampled in the Russkaya Gavan Bay (Fjord) (see table).

The floor and slopes of all the above-mentioned depressions are almost everywhere dissected by small valleys several meters to several dozens of meters deep and hundreds of meters wide. Judging from echosounding records, they alternate with swell-shaped rises of similar dimensions. The exogenic (erosional-accumulative) origin of such topography is undoubted, but its formation time is not clear. According to the continuous seismic profiling data, valleys and swells are usually reflected in the topography of the opaque layer of Upper Pleistocene glacial sediments and are enveloped by transparent or stratified sediments corresponding to deglaciation and Holocene (Fig. 2). In some cases, however, channels are incised into Holocene beds, indicating an erosional activity of bottom currents near the trough bottom (Fig. 3).

The modern hydrological situation in the Barents Sea is controlled by the influx of relatively warm and more saline Atlantic water mixing with cold and less saline Arctic water, which results in the formation of the polar Barents Sea water mass. The Atlantic water is transported from the North Atlantic by the warm surficial Norway Current, which splits into two branches north of Norway. One of them, represented by the Nordkapp Current grading into the Murmansk Current enters via the Bear Island Trough into the southern part of the Barents Sea, is traced to the western coast of Novaya Zemlya in the form of the subsurface current, and then is transformed as a result of a mixing with the Arctic water. The second branch (Western Spitsbergen Current) flows northward, bends around Spitsbergen, dips under counter flows of Arctic water, and brings subsurface Atlantic water to the Barents Sea from the north via the Franz Victoria and Saint Anna troughs.

Arctic water enters the Barents Sea with surface currents through passages between Novaya Zemlya, Franz Josef Land and Spitzbergen. It flows out in the transformed form, via the pass located south of Spitsbergen. The central part of the sea, which accommodates a cyclonic gyre formed by surface waters (Aagaard and Carmack, 1989; *Atlas okeanov...*, 1980; Hald *et al.*, 1999), is crossed in the NW–SE direction by the Polar Front. In cruises 11 and 14 of the R/V *Akademik Sergei Vavilov*, it was distinctly registered by hydrophysical sounding above the Perseus Trough, in the area of stations ASV-858 and ASV-1200. Near 76° N, a narrow flow of the relatively warm (up to 3°C) and saline (to 35‰) Atlantic water almost reaches the bottom. The flow is separated by sharp temperature and salinity gradients from the cold (below 0°C) and less saline (34.6‰) intermediate Atlantic water. A similar frontal zone is outlined in the Demed Trough area (Franz Victoria Trough), near Station ASV-880. The narrow flow of subsurface Atlantic water, which enters from the north and reaches the bottom, comes into contact with the sharp lateral temperature and salinity gradients of

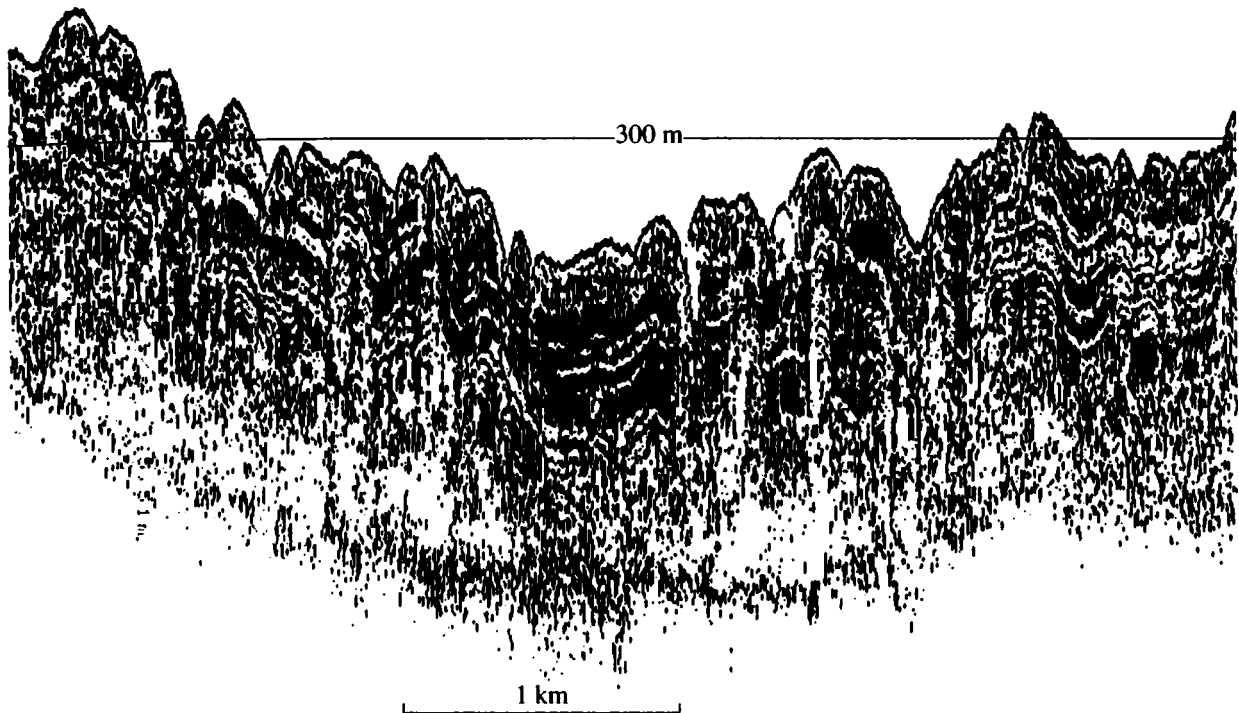


Fig. 2. Seismic record (3.5 kHz) from the southern part of the Central Deep near Station ASV-1183. Stratified layer corresponds to horizon II.

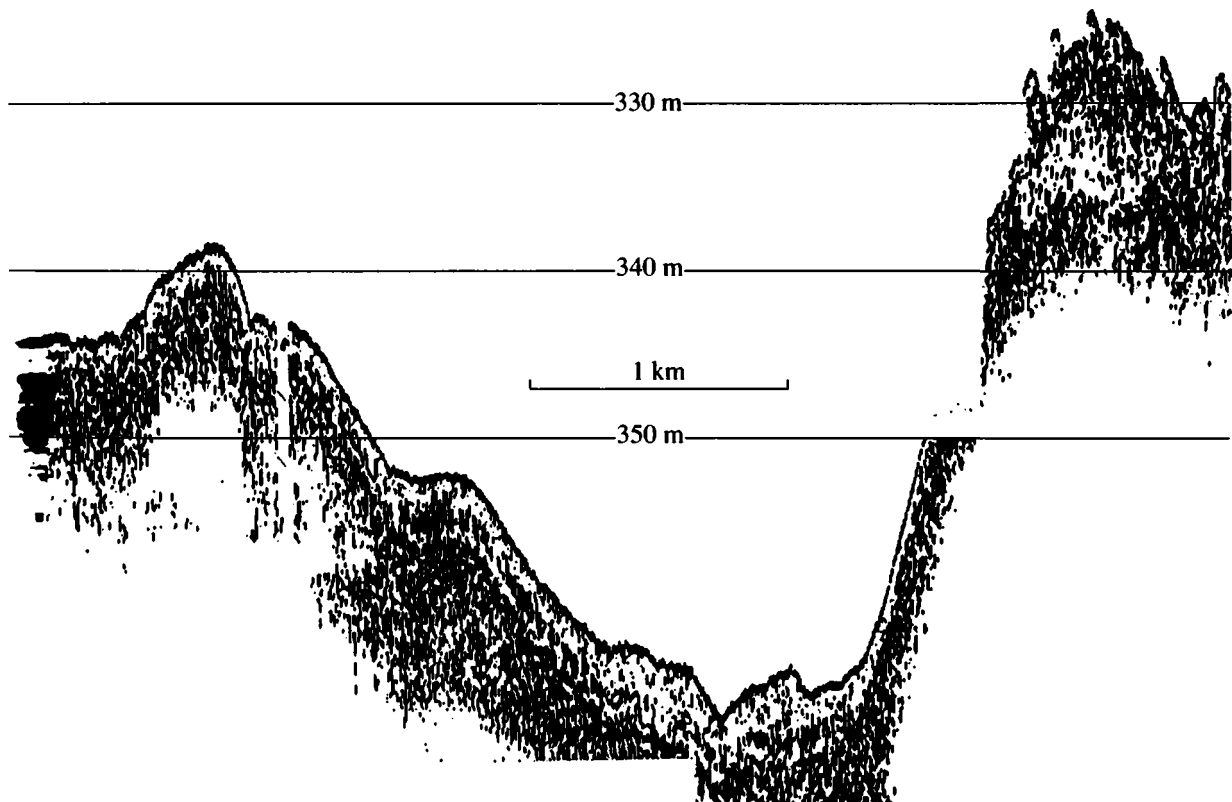


Fig. 3. Seismic record (3.5 kHz) from the Perseus Trough (Station ASV-1221 area). The thickened acoustically transparent upper layer at the bottom of a narrow valley corresponds to the Holocene.

the intermediate Arctic water. The high biological productivity characteristic of frontal zones is manifested in elevated concentrations and accumulation rates of organic matter, as well as in abundant macro- and microfossils (in more details, this phenomenon is considered below when characterizing cores ASV-880 and ASV-858).

The Barents Sea bottom is universally covered by terrigenous sediments. The terrigenous material is provided by the following main sources: (1) the solid discharge of rivers directly flowing into the sea (e.g., Pechora River) and transported in the form of suspension from the White Sea (Severnaya Dvina River) and Kara Sea (Ob, Yenisei rivers); (2) the abrasion of coasts; (3) the erosion of bottom by waves (at shallow depths) and bottom currents (at tops and on slopes of underwater rises); (4) a transport by floating ice from the Central Arctic, where ice contaminated by the terrigenous material enters mainly from the Laptev Sea (Nürnberg *et al.*, 1994); (5) a distant transport of eolian dust which spreads into the sea with snow and rain (Shevchenko *et al.*, 1999), is included into ice of glaciers of Novaya Zemlya, Franz Josef Land, Spitsbergen, and then transport into sea by thawed water of glaciers included in *glacier milk*; and (6) a transport of exaration products of cover glaciers from islands by thawed water and icebergs.

The attempts to estimate the relative input of the above-mentioned sources into the balance of the terrigenous material entering the Barents Sea (*Arkticheskii shel'f...*, 1987; Medvedev and Potekhina, 1990; Pavlidis *et al.*, 1998) revealed a significant, probably preponderant role of the finely dispersed (50–60% of fraction finer than 0.001 mm) *glacier milk* influx transported by glaciers mainly from the Severnyi Island of the Novaya Zemlya Archipelago. However, as shown in the Russkaya Gavan Bay (Aibulatov *et al.*, 1999) studies, the main bulk of this material precipitates in glacier fjords and only a small share is transported into the open sea.

The significant role in the terrigenous influx belongs to the fine suspended material entering via the neck of the White Sea and also belongs to products of coastal abrasion (*Arkticheskii shel'f...*, 1987; Pavlidis *et al.*, 1998).

The suspended terrigenous material is distributed throughout the sea mainly through two water layers of the elevated turbidity: the surface (above pycnocline) and bottom layers (Aibulatov *et al.*, 1999). Precipitation of suspension from the surface layer, where its concentration averages 2–5 mg/l, occurs mainly in accordance with the hemipelagic mechanism of biofiltration (pellet) sedimentation, thus, depending on bio-productivity of waters. The lateral transport and redeposition of the fine terrigenous material occur in the bottom nepheloid layer and are controlled by bottom currents. The latter, in turn, depend on the bottom topography; in profiles of the turbidity distribution, the

nepheloid layer (an elevated density determined by the low temperature and high salinity of waters, as well as by concentration of suspension) runs down along the slopes of underwater rises to shelf depressions (Aibulatov *et al.*, 1999), which results in accumulation of fine-grained sediments (see below).

The sandy and coarse detrital material is transported to the open sea by icebergs and floating ice, including pack ice (Nürnberg *et al.*, 1994). The modern ice rafting of the coarse detrital material by icebergs is confirmed by our observations; at some sites in the northern part of the Central Deep, abundant rock boulders and pebbles were dredged by trawl from the surface of Holocene fine-grained sediments. Many boulders bear glacial striation. The petrographic composition of rocks is variable, which is also characteristic of the ice-rafted material. The possibility of the modern ice rafting is confirmed by observations of iceberg drift (Afanas'ev and Voevodin, 1996; Aksenov and Pozdnyshev, 1996).

LITHOLOGY AND STRATIGRAPHY

The cores taken in cruises ASV-11 and ASV-14 recovered (completely or partly) the three-member section (Fig. 4) typical of the Barents Sea, often described in different publications (for instance, Murdmaa *et al.*, 1997, 1998a; Pavlidis *et al.*, 1998; Polyak and Solheim, 1994). Three lithostratigraphic horizons are distinguished in the section based on lithological, micropaleontological and geochemical features (from the base upward).

Horizon III is composed of uniform in coloration, dark-gray sandy-silty-clayey mud with dispersed gravel and pebbles (shingle). In recent publications (Hald *et al.*, 1999; Polyak and Solheim, 1994; Polyak *et al.*, 1995; 1997), this horizon is usually described as diamicton. The content of sand, gravel, and coarser (to 10 cm) fragments in the latter is significantly higher than in both overlying horizons. Nevertheless, the pelitic component is similarly fine and is dominated by the clayey fraction less than 0.001 mm. This fact was previously noted by other researchers (for instance, Pavlidis *et al.*, 1998). The granulometric spectrum is bimodal, with peaks in the area of sandy and pelitic fractions. The structure is massive, with no signs of the material transport by gravity flows. Gray coloration of sediments indicates the reductive character of early diagenesis, but hydrotroilite is missing. N.V. Pimenov's data (Murdmaa *et al.*, 1997) show that the salinity of reconstructed bottom water, on the basis of chlorine content in interstitial water, is usually lowered (28–31‰), but not lower than values characteristic of slightly fresh-water marine basins. According to Gordeev's determinations, the organic carbon content is low. Sediments are characterized by the sufficiently high content of pelitomorphous, most likely authigenic (diagenetic) carbonate and the presence of pyrite.

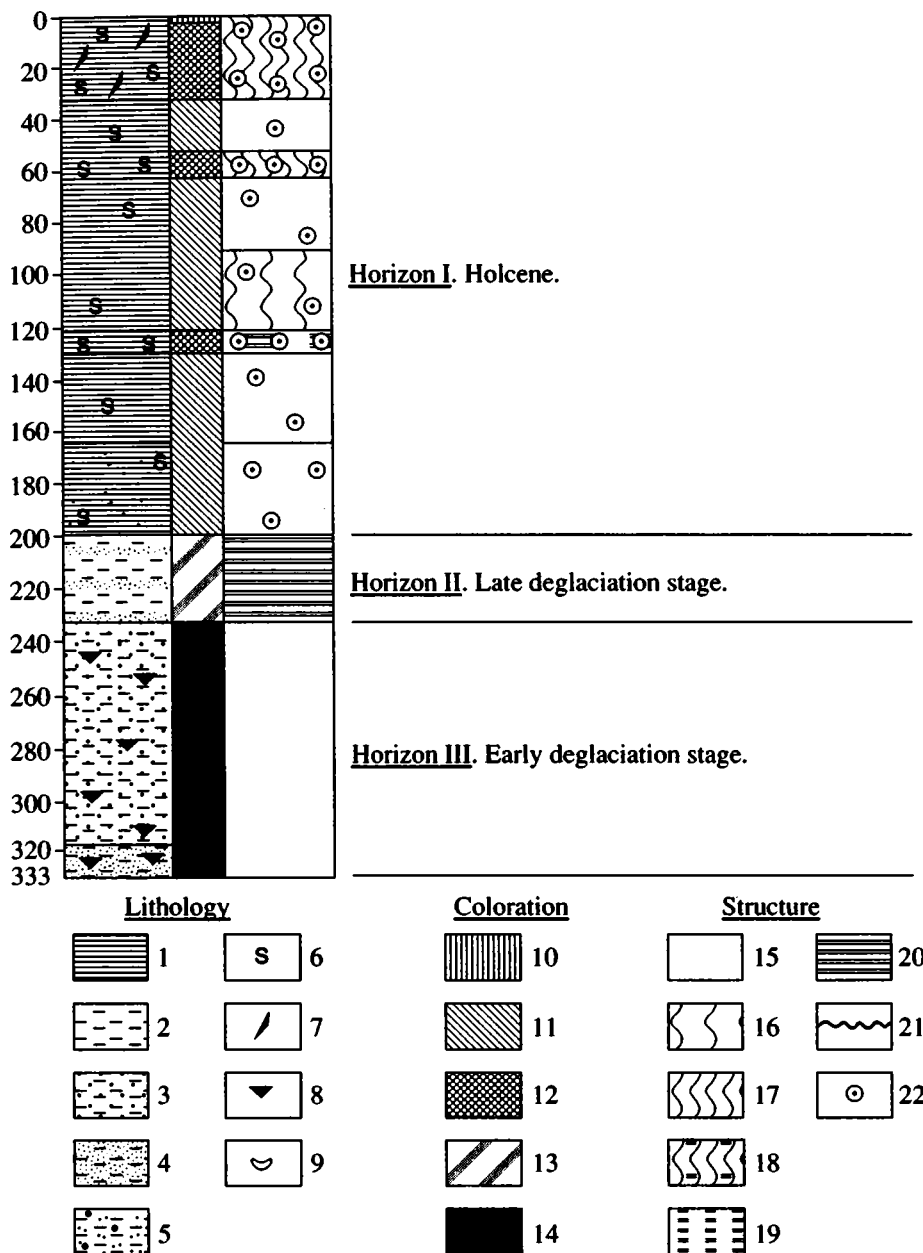


Fig. 4. The type section of postglacial sediments of the Barents Sea (Core ASV-1200, Perseus Trough). Lithology: (1) clayey mud, (2) silty-clayey mud, (3) silty-clayey mud with sand, (4) sandy-silty-clayey mud; (5) diamicton (pebbly loam); inclusions: (6) hydrotroilite, (7) Polychaeta tubes, (8) pebble, shingle, (9) molluscan shells; sediment coloration: (10) brown, (11) olive-gray, (12) dark olive-gray, (13) variegated, (14) gray, dark-gray; (15) homogeneous structure; bioturbation: (16) slight, (17) intense, (18) with obscure bedding; (19) obscure lamination; (20) parallel lamination; (21) cementation crust (hardground); (22) mottled.

The gray clay horizon encloses shells of Pleistocene planktonic (*Neogloboquadrina pachyderma* (Ehrenberg) and benthic (*Elphidium excavatum* forma *clavatum* Cushman, *Cassidulina reniforme* (Norvang), and others) foraminifers, as well as well-preserved fragile aragonite shells of planktonic mollusks, pteropod species *Limacina helicina* (Phipps) dwelling in moderate and high-latitude areas (Be and Gilmer, 1977). Rare shells of reworked Mesozoic and Cenozoic foraminifers

are also noted. However, many samples are lacking microfossils. Nonetheless, the occurrence of specimens of Recent well-preserved foraminiferal and pteropod species indicates the existence of marine sedimentation environments.

Sediments of horizon III differ from overlying sediments in a higher density and lowered moisture content. According to our observations, however, a sharp jump in a density at the contact between horizons II and

III occurs only in some areas. In several cores, the transition is sufficiently smooth with a gradual increase of the density downward. In Core ASV-1221, where horizon II is missing, the surface of horizon III represents a ferruginous hardground (cementation crust) that marks a break in sedimentation or erosion.

The apparent thickness of horizon III recovered by cores does not exceed 2.5 m (Table). The horizon is completely penetrated only by Core ASV-880, where it is 0.9 m thick and underlain by a very compact dark-gray pebbly loam, probably of the moraine origin (horizon IV). In seismic records, the distinct reflector is registered at the top of horizon III, and its upper surface is usually characterized by a sharply differentiated topography (Figs. 2, 3). The age of horizon III is not established and can hardly be established by presently-used methods. Judging from the radiocarbon dates for the base of horizon II in the Franz Victoria (Polyak and Solheim, 1994) and Saint Anna (Hald *et al.*, 1999; Polyak *et al.*, 1997) troughs, the age of gray clay is older than 13 ka (i.e., 15200 calendar years). The age is > 12 ka in the Bear Island Trough (Elverhøi and Solheim, 1983).

Based on the cited data, we believe that horizon III was deposited under conditions of a slightly fresh-water (at the expense of the influx of thawed water from glaciers) basin. The considered sediments represent proximal glaciomarine deposits accumulated during the early deglaciation stage under influence of ice rafting of the clastic material and precipitation of fine-grained *glacier milk* transported by thawed water of retreating glaciers.

Horizon II is recognized as an intermediate layer between the lithologically distinct horizons III and I. Its lithological characteristics and thickness are variable in different areas. The criterion for distinguishing this horizon is due to the appearance of brownish, yellowish, and pinkish sediments in the section, which indicates oxidizing environments, as well as bedded and laminated structures, the absence of bioturbation and signs of sulfate-reduction (hydrotroilite).

In some cores from the central and northern parts of the sea (ASV-858, ASV-861, ASV-897, ASV-1200, ASV-1212, ASV-1213, ASV-1217, ASV-1282, ASV-1302, ASV-1310), the horizon is composed of alternating sediments variable in granulometric composition (from clayey to silty-clayey muds with a sand admixture in some laminae and even to sand in Core ASV-1310) and coloration (brown, brownish gray, rusty-brown, gray, and dark-gray). Remarkable are intervals with distinct parallel, both thick (centimeter-scale) and thin (millimeter-scale) lamination, which is manifested in alternating brown (oxidized) and gray (reduced) laminae. No bioturbation signs are observed. Similar laminated sediments are recorded in the Franz Victoria (Libinski *et al.*, 1996; Polyak and Solheim, 1994) and Saint Anna (Hald *et al.*, 1999; Polyak *et al.*, 1997) troughs, as well as in the southeastern part of the sea (Polyak and Mikhailov, 1996).

In other cores from the northern part of the sea (ASV-875, ASV-877, ASV-880, ASV-883, ASV-902), horizon II is represented by uniform, massive, yellowish gray, pinkish gray or greenish gray silty-clayey mud, which differs from underlying and overlying sediments in the elevated moisture content and peculiar oily consistence. Uniform brownish intervals occur within the considered horizon along with laminated interval in some above-mentioned cores (ASV-861, ASV-1310, and others).

The top of horizon II in some cores is marked by the rusty-brown compact bed representing a hardground. The upper surface of the crust is usually uneven and sometimes obliquely oriented relative to the bedding resembling erosion surface. In Core ASV-1221, horizon II reduces in thickness to the rusty-brown oxidized crust 2–3 cm thick and rests upon the upper surface of horizon III. The lower boundary of horizon II is sharp and usually marked by the change in coloration, by the density increase, and by coarser sediments. In some cases, however, the boundary interval is represented by alternating sediments with lithological characteristics of both horizons.

Core ASV-1183 from the southern part of the Central Deep recovered uniform brownish gray pelitic mud with an apparent thickness of 154 cm and overlain by typical Holocene sediments. Based on stratigraphic position and brownish coloration of sediments, they are arbitrarily referred to horizon II.

Core ASV-1060 from the eastern part of the Central Deep, at a continuation of the Western Novaya Zemlya Trough, recovered an interval (34 cm) with gradation bedding and resembling turbidite cyclite below the 1.5-m-thick Holocene horizon. The interval base is marked by a massive sandy-silty bed (2 cm) grading upward into the laminated interval (12 cm) of alternating clayey and silty laminae. In the higher section, there is a layer (6 cm) of gray silty-clayey mud with abundant dark-gray lentils (possibly, intraclasts) of compact lumpy sandy-silty sediment with green glauconite-like aggregates. The cyclite terminates with a homogenous dark-gray clayey mud layer 14 cm thick. The upper contact is distinct and slightly wavy.

The turbidite cyclite rests on a dark-gray pelitic mud layer that contains scattered yellowish interbeds in its upper part, whereas its lower part is marked by vertically oriented large rock fragments probably indicating a transition to glacial diamicton (till) horizon or to gravity-flow sediments. We refer turbidite and underlying clays with yellowish intercalations to horizon II, whereas the stratigraphic position of underlying sediments is not clear. Lithologically similar turbidites were previously reported from the basal part of the Holocene sediments in cores from the eastern part of the Central Deep (Gataullin *et al.*, 1993; Kalinenko, 1985; Polyak and Mikhailov, 1996).

Microfossils are characterized by a low diversity and an extremely low abundance (except for some sam-

ples) of benthic, mainly secretory foraminifers and single planktonic foraminifers that are represented by one or two species. Preservation is variable. Most common are *Elphidium excavatum* forma *clavatum* and *Cassidulina reniforme*. Foraminifers are missing in most cores, which prevent detailed subdivision of this sequence. However, there are single specimens of forms that Korsun *et al.* (1994) relate to the Atlantic water: *Cassidulina teretis* Loeblich and Tappan, *Pullenia bulloides* (d'Orbigny), *Cibicides wuellerstorfi* (Schwager). Reworked specimens of secretory Cenozoic and agglutinated Mesozoic foraminifers are less abundant. Mostly good preservation of Recent species and data on paleosalinity of interstitial water (Murdmaa *et al.*, 1997, 1998b) indicate that sediments of the horizon were accumulated in marine environments during the terminal stage of deglaciation. The lowered paleosalinity of interstitial water (30–32‰), as compared with the modern one, suggests freshened bottom water. However, some cores (for instance, ASV-858 described in detail below) show intervals with the elevated salinity within this horizon. In seismic records, the horizon is marked by laminated patterns enveloping uneven surface topography of the underlying horizon (Fig. 2).

An age of sediments composing horizon II is yet to be determined. This task is strongly impeded by the rare occurrence of carbonate molluscan, gastropod, ostracod, and foraminifer shells. Single radiocarbon dates, obtained for the basal sediments of the similar layer in the Franz Victoria Trough and in the southeastern part of the Barents Sea published in some works (Lubinski *et al.*, 1996; Polyak and Mikhailov, 1996; Polyak and Solheim, 1994), yielded an age of 13 ka. According to data of the cited authors, the age of the base of the overlying Holocene horizon is estimated to be 10–9.5 ka.

Variations in the thickness of horizon II in the studied depressions are given in the Table and exemplified by the profile along 42° E (Fig. 5).

Horizon I is composed of clayey and silty-clayey olive-gray to dark-olive gray mud with black spots enriched in hydrotroilite that emphasizes the bioturbation structure. The section usually consists of obscure layers containing fucoids and variable hydrotroilite content; their thickness ranges from several centimeters to several dozens of centimeters. In some cores, the section of horizon I is divided into the upper and lower parts differing in bioturbation patterns and the form of hydrotroilite segregations. In the upper part, hydrotroilite is perceived as large spots, which mark fucoids. In the lower one, they have small punctuation or have the form of strokes subparallel to bedding.

Surface sediments are usually penetrated by Polychaeta tubes to the depths of 10–30 cm, sometimes, deeper. Judging from grab samples, the top of horizon I universally corresponds to the brown oxidized layer of semiliquid mud 1–3 cm thick (rarely to 6 cm), probably

representing an ephemeral warp that is intermittently roiled by bottom currents. In the course of coring, this layer is usually destroyed or washed out.

Holocene sediments are characterized by high lateral and temporal variations in composition of faunal assemblages and their preservation. In some cores, intervals barren of fossils or containing very rare fossils alternate with intervals, which enclose diverse (more than 20 species) but not numerous assemblages or diverse (15–22 species) and sufficiently abundant benthic (mainly secretory) foraminifers. Planktonic foraminifers occur as single specimens. In other cores, diverse (up to 24 species) and abundant benthic foraminiferal assemblages occur throughout the entire Holocene section. Preponderant are *E. clavatum* and *C. reniforme*; common are also *Islandiella helenae* Feyling-Hanssen et Buzas, *Islandiella norcrossi* (Cushman), *Buccella* spp., *Elphidium subarcticum* Cushman, *Cibicidoides lobatulus* (Walker et Jacob), and planktonic form *Neogloboquadrina pachyderma* sin. Some intervals show the presence of *Melonis barleeanus* (Williamson), *Cassidulina teretis*, both characteristic of Atlantic water, and *Nonion labradoricum* (Dawson) which is abundant in the Polar Front zone (Hald and Korsun, 1997; Polyak and Solheim, 1994). The pteropod species *Limacina helicina* of sufficiently good preservation are present as single specimens. Sometimes, the foraminiferal abundance shows strong variations even in neighboring cores located only two miles apart.

The abundant Recent fauna, the presence of hydrotroilite, the very low content of the coarse ice-rafted material, and the normal salinity of interstitial water reflect environments of marine sedimentation close to the modern ones and allow horizon to be referred to the Holocene. According to radiocarbon dates (Hald *et al.*, 1999; Lubinski *et al.*, 1996; Polyak and Mikhailov, 1996; Polyak and Solheim, 1994), the age of the base of the first horizon is 10–9.5 ka (i.e., 11 000–12 000 calendar years).

Based on different microfossil groups, horizon I is subdivided in different cores into several intervals correlating with the climatic phases of the Holocene (Polyak and Mikhailov, 1996; Polyak and Solheim, 1994; Samoilovich *et al.*, 1993).

In the case of low thickness (to 2–3 m), the Holocene horizon is reflected in seismic records as an acoustically transparent layer (Fig. 3), whereas in the case of their high thickness, an interference layering is observed (for instance, in lithologically uniform Core ASV-987 from the Russkaya Gavan area).

The thickness of the Holocene horizon in cores under consideration varies from 12 to 389 cm (table). In some cores from the Western Novaya Zemlya Trough and Russkaya Gavan Bay, the apparent thickness of this horizon exceeds 500 cm. According to the isopach map compiled by Gurevich (1995, Fig. 3.2, p. 20), the thickness of the Holocene horizon in depressions of the open

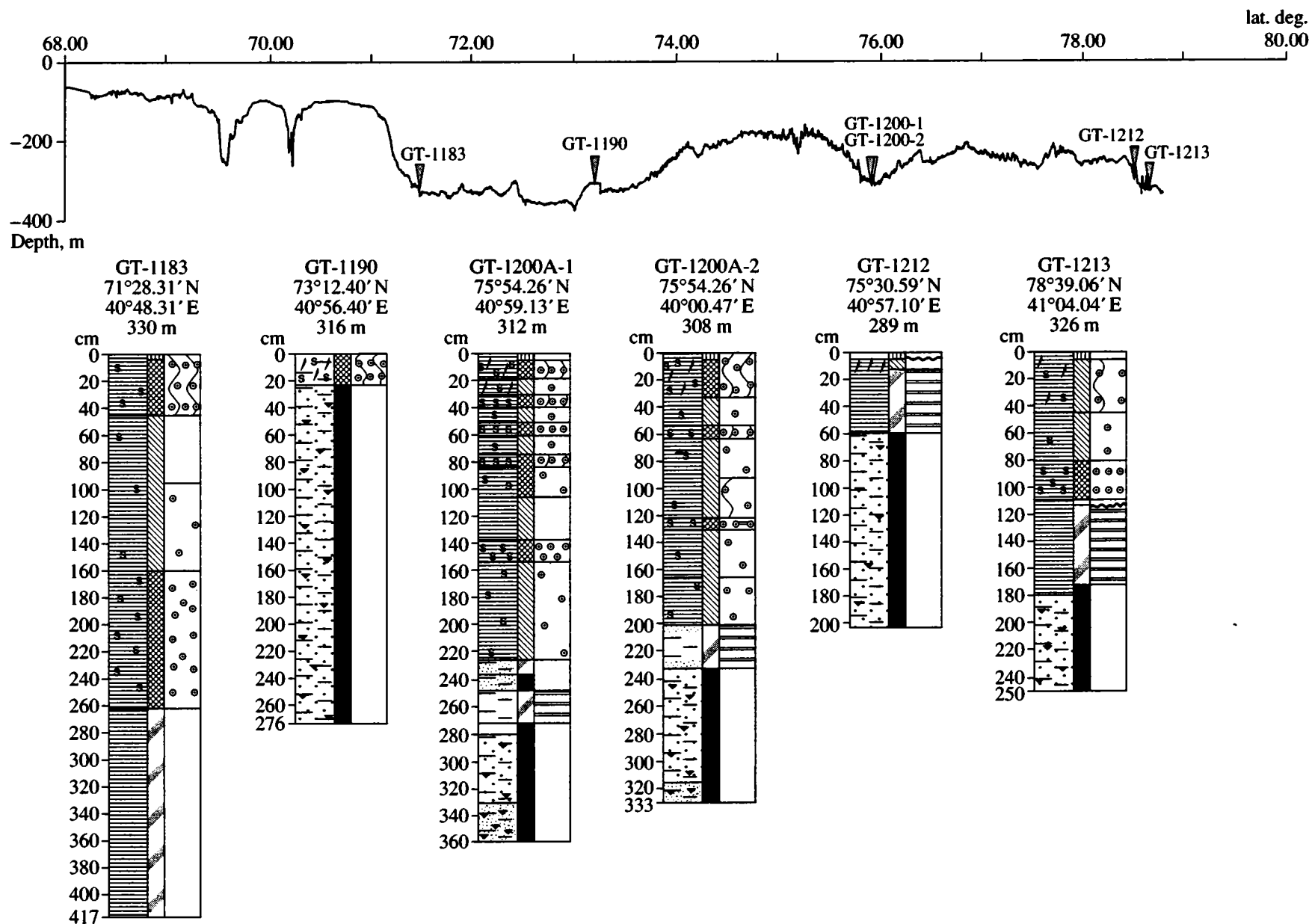


Fig. 5. Stratigraphic subdivision of cores taken along the meridional profile at 41°E. For legend see Fig. 4.

part of the Barents Sea ranges from 0.1–1 m to 1–5 m, which agree well with our data. Variations in the thickness of Holocene sediments are exemplified by the meridional profile along 42° E (Fig. 5).

SECTIONS OF THE FRANZ VICTORIA AND PERSEUS TROUGHS

The Franz Victoria Trough, located between the Franz Josef Land and Spitsbergen archipelagoes, and where the thoroughly studied Core ASV-880 was taken (Fig. 6), is of a key importance for paleoceanographic reconstruction representing one of paths for penetration of Atlantic water into the Barents Sea (Polyak and Solheim, 1994). The area above the Perseus Trough, near the site where Core ASV-858 was obtained, is now crossed by the Polar Front zone. Therefore, the section of the core allows the history of the interrelation between Atlantic and Arctic waters in the central part of the sea to be deciphered.

Core ASV-880 was taken at the depth of 388 m from the floor of the narrow Demed Trough between the socle of the Franz Josef Land and the underwater Demed Rise (Fig. 1). Judging from the hydrophysical sounding data, this area is crossed by the flow of subsurface Atlantic water entering the Demed Trough from the north and reaching the bottom of the trough. In the east, it is separated by a zone with sharp temperature and salinity gradients from cold slightly freshened Arctic water that produces an effect of the frontal zone. The zone of high bioproductivity is probably confined to the latter. The seismic record reveals an increase in the thickness of the upper transparent layer (corresponding to the Holocene) in the axial part of the depression and its wedging out at flanks of the latter.

The three above-described stratigraphic horizons are distinctly recognized in the core section; their boundaries are located at 310, 405, and 494 cm. The basal layer of the section (494–508 cm) is composed of pebbly loam (true diamicton) probably representing a moraine (Fig. 6, horizon IV). This is a very compact, almost dry (the moisture content is 19%), dark-gray, unsorted sediment composed of an irregular mixture of clay and detrital material of silt to pebble (to 10–12 cm) dimension. The moraine origin of basal sediments is confirmed by the absence of fossils (only single specimens of *Neogloboquadrina pachyderma* sin. are recorded) and low salinity of interstitial water (13‰, Murdmaa *et al.*, 1997).

Sediments from Core ASV-880 are characterized by the decrease in the size of the detrital material upward to the section from the basal moraine layer (horizon IV) to the Holocene (Fig. 7). The sandy-gravelly material (the content of the fraction coarser than 0.1 mm exceeds 50%) is preponderant in moraine. Nonetheless, there is another peak in the area of the fine pelitic material (fraction finer than 0.005 mm). In all of the overlying horizons, sediments are dominated by the fine-pel-

itic fraction, whose content grows upsection from 55% in horizon III, to 65% in horizon II, and to 75% in horizon I. The proportions of fractions within the fine-grained part of the spectrum remains stable and indirectly confirm the homogeneous nature of sediments. Simultaneously, horizons III and II yield a second peak into the granulometric spectrum in the area of sand and gravel indicating their different (probably iceberg-related) origin. Strong peaks of coarse fractions with the distinct preponderance of sand over coarse silt occur in horizon II, suggesting the presence of sandy beds probably related to the activity of bottom gravity flows (Fig. 6).

Unlike in other cores, horizon II is represented in the considered section by uniform greenish gray clayey mud barren of hydrotroilite; the content of organic matter is relatively low (1.0–1.5%). The first half of the Holocene is characterized by the elevated content of the sandy-gravelly fraction (Fig. 6). In our opinion, this fact indicates a more intense iceberg-related rafting, as compared with the present-day process. In the lower part of the Holocene section, the C_{org} content is lower (about 1.5%) than its upper portion (approximately 2%) content. However, lower Holocene sediments are more rich in hydrotroilite.

Microfossils are sufficiently rare in horizons III and II, where they are represented by Recent and reworked, mainly benthic, Mesozoic and Cenozoic foraminifers of variable appearance (from perfectly preserved to recrystallized). Recent forms are represented by *Elphidium* spp., *Cassidulina reniforme*, *Islandiella norcrossi*, *Haynesina orbiculare*, *Cibicides lobatulus*, and others. Planktonic foraminifers (*Neogloboquadrina pachyderma* sin.) and mollusks occur as single specimens. Sediments of horizon II yields, in addition to the above-mentioned forms, rare secretory benthic and planktonic species characteristic of the North Atlantic, particularly of the Norwegian Sea: *Pullenia bulloides*, *Cibicidoides wuellerstorfi*, *Cassidulina tereitis*, *Melonis batleeanus*, *Neogloboquadrina pachyderma* dex., *Turborotalita quinqueloba* (Natland) of mostly good preservation.

Most abundant and diverse are foraminifers in the Holocene sediments, where single shells of pteropods (*Limacina helecina*), bivalves, gastropods, and ostracods are also present. The horizon is marked by a change in the role of dominant benthic secretory foraminifer species *Cassidulina reniforme* and *Elphidium clavatum* (Fig. 6). In the middle part of the horizon, the latter species is close in abundance to other dominant species *Cassidulina reniforme* and *Buccella* spp. and sharply prevails only in the upper part. Preservation of planktonic and benthic foraminifers varies even within the same samples; some samples are barren of foraminifers due to dissolution.

The abundance of planktonic foraminifers represented by one–two species insignificantly varies within the horizon (from 0 to 16 specimens/g of dry sediment),

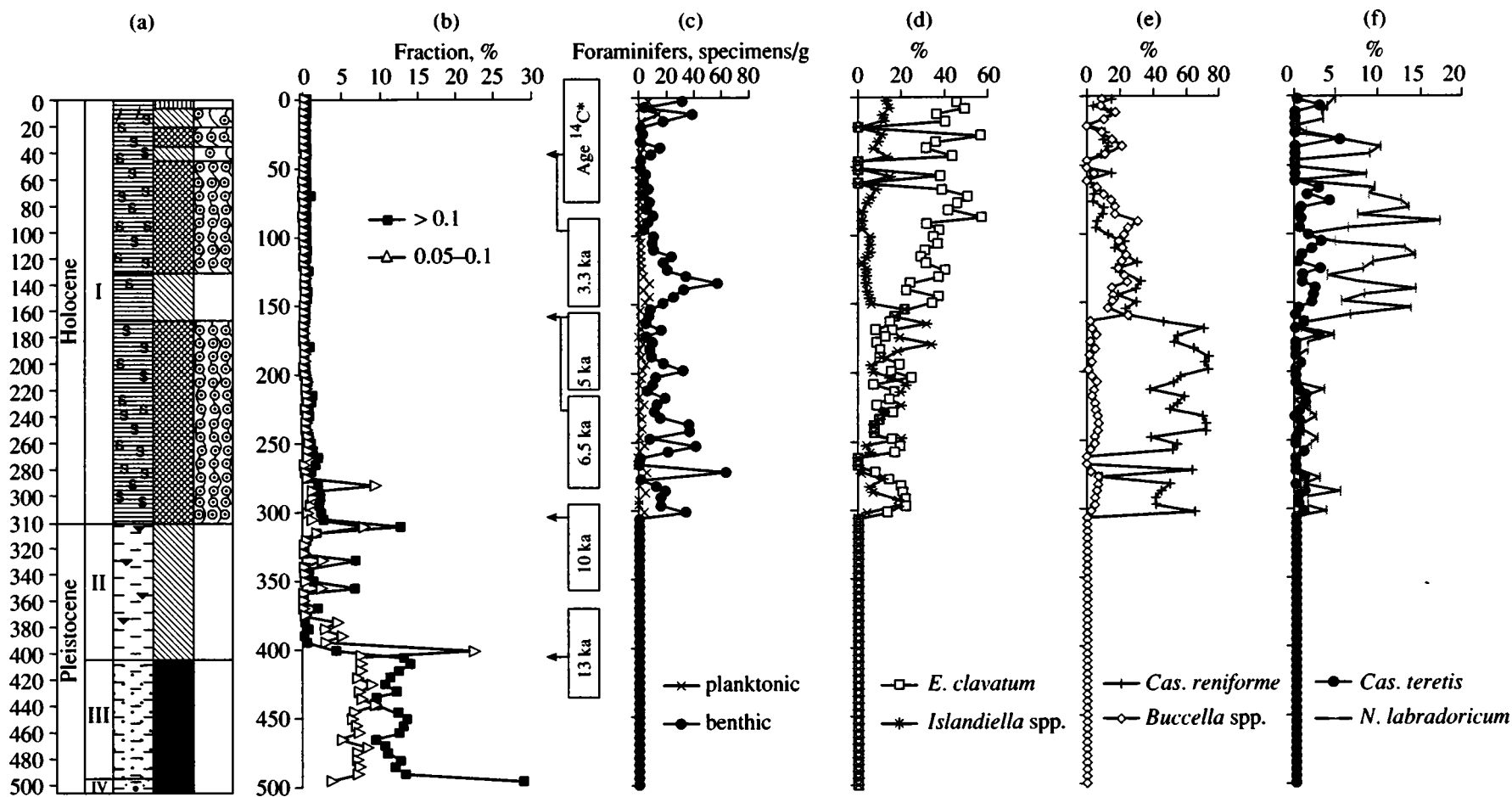


Fig. 6. Core ASV-880 (Franz Victoria Trough). Radiocarbon dates (ka) in plots of the relative content dominant and indicative foraminiferal species are extrapolated using data from Cores P1-91-AR-JPC5 (Lubinskii *et al.*, 1996) and 32 (Polyak and Solheim, 1994). For lithological symbols see Fig. 4.

whereas that of benthic forms ranges from 1 to 66 specimens/g. Amid planktonic species, *Neogloboquadrina pachyderma* sin. is preponderant; boreal forms *N. pachyderma* dex. and *Turborotalita quinqueloba* occur as single specimens. Secretory benthic foraminifers sharply prevail over planktonic forms throughout the entire horizon, as well as over agglutinated benthic species, whose shells rapidly disintegrate in the course of sediment diagenesis (Hald and Korsun, 1997; Hald *et al.*, 1999; Polyak and Solheim, 1994).

The diversity of benthic foraminifers varies from 6 to 23 depending on changes in dwelling and burial conditions. The replacement of *Cassidulina reniforme*, as a dominant element of the assemblage by *Elphidium clavatum*, corresponds with a significant increase in the content of *Nonion labradoricum*, whose distribution is related, in opinion of some researchers, to the elevated bioproductivity. Simultaneously, the abundance of the *Cassidulina teretis* characteristic of the Atlantic water and the *Melonis barleeanus* typical of the zone of mixed Atlantic and Arctic waters also increases (Hald *et al.*, 1991; 1994; Lubinski *et al.*, 1996; Polyak and Solheim, 1994).

Thus, three distinct intervals with different foraminiferal assemblages can be distinguished in the Holocene sediments. The correlation of separate peaks of the elevated content of the above-mentioned secretory species, with similar dated peaks in cores P1-91-AR-JPC5 (Lubinski *et al.*, 1996) and 32 (Polyak and Solheim, 1994) from the same area, allows the age of these intervals to be estimated (Fig. 6). According to the relationship of the three most representative species and sediment lithology, the considered horizon corresponds to the upper horizon of Core P1-91-AR-JPC5 composed of olive-gray silty clay. The radiocarbon age of the lower boundary of the horizon is about 10 ka.

Core ASV-858 is taken in the Perseus Trough at a depth of 312 m. The section is represented by three above-described horizons, boundaries between which occur at depths of 200 and 256 cm bsf (Fig. 8). Similar to Core ASV-880, the decrease tendency in the content of a coarse material upward to the section is preserved also in this core, although the relations between fractions significantly differ (Fig. 7). The remarkable feature is a preponderance of coarse silt over the sandy-gravelly material and significantly higher content of fine silt fraction (0.05–0.1 mm). The fraction content finer than 0.005 mm is substantially lower. As a result, bimodal patterns of the granulometric spectrum are not observed in the horizons. The granulometric spectrum of horizon III in the considered core differs from that in the same stratigraphic horizon of Core ASV-880, which is first reflected in the prevalence of coarse silt over sandy-gravelly fraction (Figs. 6, 8). The upper part of horizon III is enriched in larger (pebble-size) fragments. The contact between horizons III and II is marked by the coarse silt layer. Horizon II is represented by laminated silty-clayey mud. Lamination is

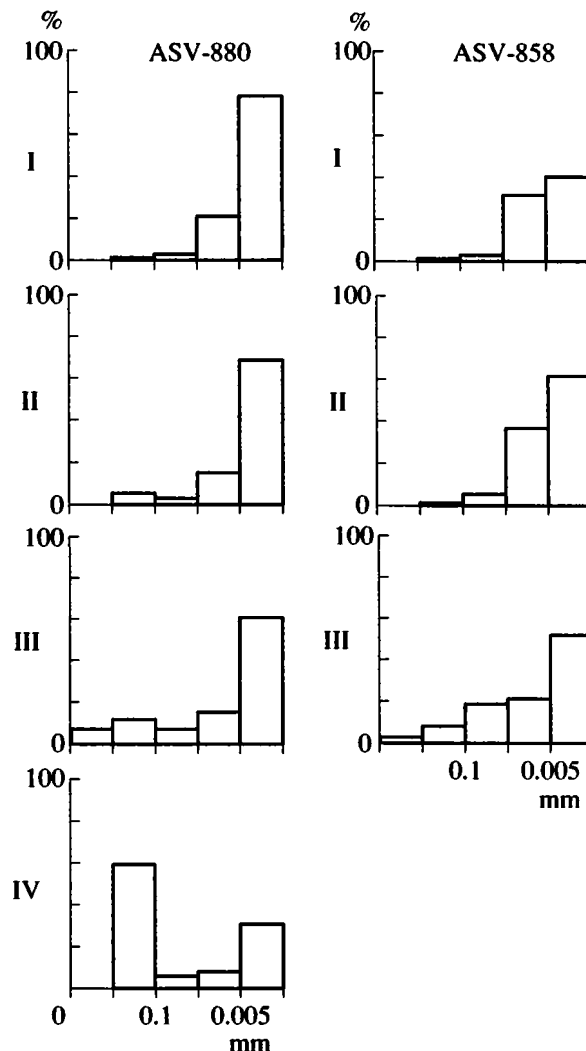


Fig. 7. Examples of histograms demonstrating a granulometric spectrum of sediments from different horizons (I–IV) in cores ASV-880 (Franz Victoria Trough) and ASV-858 (Perseus Trough).

formed by alternating millimeter-scale brownish and bluish laminae. Bioturbation is absent.

Unlike in most of the cores, the middle part of the horizon in the considered core is characterized by elevated (to 34‰) salinity of interstitial water and by the relatively high C_{org} content (about 2%). This anomaly probably reflects the development of the frontal zone with participation of more saline Atlantic water.

The lower part of the Holocene horizon differs from its upper portion in the elevated content of coarse silt. The higher content of fine silt and coarse pelite (0.05–0.005 mm) most likely indicates a bottom sediment reworking by nepheloid flows. The content of hydrotroilite is generally lower than in Core ASV-880; the lower part of the Holocene horizon is virtually barren of hydrotroilite.

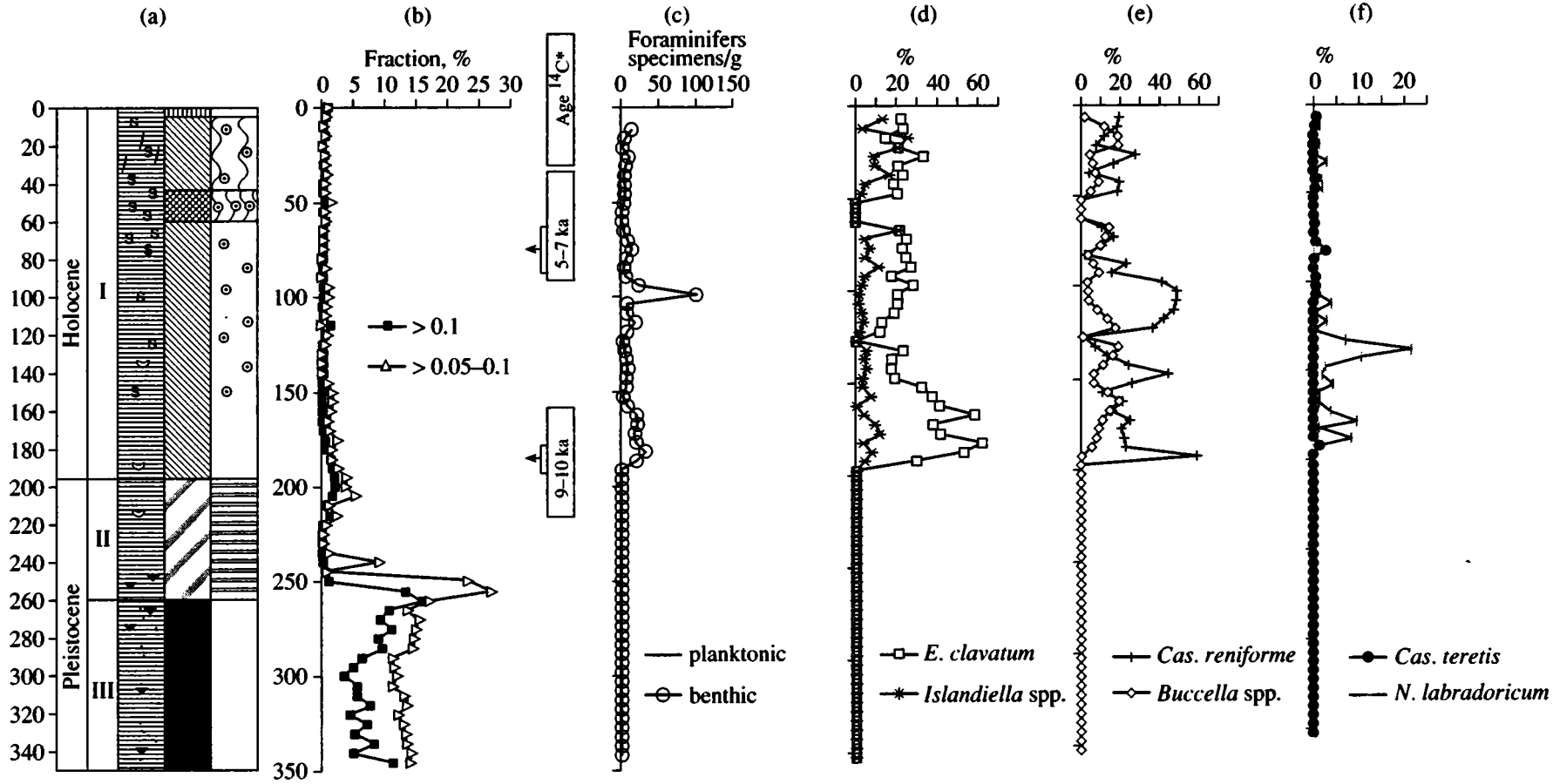


Fig. 8. Core ASV-858 (Perseus Trough). Radiocarbon dates (ka) in plots of the relative content of dominant and indicative foraminiferal species are extrapolated using data from (Polyak and Mikhailov, 1996). For lithological symbols see Fig. 4.

The fossils of horizons III and II are represented by Recent variably preserved planktonic and benthic foraminifers that belong to the same species as in Core ASV-880 and by reworked Mesozoic forms. Horizon III yields single specimens of pteropod *Limacina helicina*.

Holocene foraminiferal assemblages of separate samples include 14–27 benthic and one planktonic species. The abundance of benthic foraminifers does not exceed 20 specimens/g and that of planktonic forms, 3 specimens/g. An exception is the interval of 95–100 cm in the lower part of the horizon, which is marked by a small abundance peak (Fig. 8). Secretory benthic forms prevail over agglutinated benthic and planktonic species throughout the entire horizon. In some samples, foraminifers occur as single specimens as a result of dissolution. The occurrence of the dissolution intervals in Holocene sections is characteristic of the entire sea and particularly for the Central Deep (Polyak and Mikhailov, 1996).

In the lower part of the horizon, *Cassidulina reniforme* and *Elphidium clavatum* are preponderant, whereas in its upper portion, species *E. clavatum*, *E. subarcticum*, *Islandiella norcrossi/helenae*, *C. reniforme*, and *Buccella* spp. are present in approximately equal proportions.

With respect of ecology, the rare and important species *Cassidulina teretis*, *Nonion labradoricum*, and *Melonis barleeanus* also demonstrate variations in the relative abundance, which can be correlated with radiocarbon-dated peaks in their relative content in sections from the southeastern part of the sea, particularly with those in the lower part of the considered horizon (Polyak and Mikhailov, 1996).

The age of sediments from the interval of 70–90 cm in the middle part of the horizon can only arbitrarily be estimated as 7–5 ka (Fig. 8) taking into consideration the abundant peaks of *Buccella* spp., *Islandiella* spp., and *Melonis barleeanus* cited in the above-mentioned publication. Such correlation, as well as the correlation of the replacement of dominant species in cores ASV-858 and ASV-880 and an absence of a peculiar maximum of agglutinated foraminifers in the upper part of the horizon (Hald *et al.*, 1999), suggest that the upper interval corresponding to the Late Holocene is characterized by the reduced thickness.

PALEOCEANOGRAPHIC ENVIRONMENTS

Three distinct stratigraphic intervals in the section of the Upper Quaternary sedimentary cover of the Barents Sea reflect three stages of the postglacial history of the basin separated from each other by short-term events of the cardinal transformation of the sedimentation system.

The beginning of deglaciation of the last glacial period is marked by the transition from moraine pebbly loam (diamicton) of the horizon IV to glaciomarine

sediments of horizon III in Core ASV-880. The genesis and formation environments of horizon III, characterized by the universal distribution in the Barents Sea, remain debatable. Many researchers consider these sediments as representing glacial diamicton, a type of bottom moraine (till) that was formed during the last glacial maximum as a result of the exaration-accumulative activity of the continuous, ground-resting Barents Sea ice shield (Dibner *et al.*, 1978; Gataullin *et al.*, 1993; Hald *et al.*, 1999; Polyak and Solheim, 1994; Polyak *et al.*, 1995, 1997).

We consider sediments of horizon III as proximal glaciomarine (mainly iceberg-related) contrary to the underlying glacial sediments (tills). This interpretation is based on the following features: (1) the high content of the clayey fraction typical of glacial sediments (bottom moraine); (2) dark-gray coloration indicating reducing environments at the early diagenetic stage; (3) good preservation of shells of Recent planktonic and benthic foraminifers as well as pteropods, which could hardly be probable in the exarating activity of glacier and erosion of older marine sediments; and (4) typical, although lowered, marine salinity of interstitial water. The occurrence of reworked Mesozoic and Cenozoic microfossils in sediments is probably related to the erosion of moraines or sedimentary rocks by under-glacier flows of thawed water. The good preservation of Recent foraminiferal species contradicts the hypothesis (Polyak and Solheim, 1994) that they were reworked from older marine sediments.

We refer the recovered part of horizon III to the early stage of deglaciation that was accompanied by the mass breaking off of icebergs from the marginal part of retreating ice shields. Consequently, the depressions in the Barents Sea bottom were already free of the ice shield by that time (13–15 ka ago), represented marine basins that were slightly freshened (at the expense of thawed water of retreating glaciers), and connected via deep troughs (Bear Island, Franz Victoria, Saint Anna) with ocean, from where relatively warm and saline Atlantic water entered. According to some data (Hebbeln *et al.*, 1994; Jones and Keigwin, 1988; Knies *et al.*, 1999; Sarnthein *et al.*, 1995; Vørren *et al.*, 1988), Atlantic water entered the Arctic Ocean north of Spitsbergen even during the last glacial maximum. Its influx into the Barents Sea via deep troughs (13 ka ago, according to the radiocarbon scale, Lubinski *et al.*, 1996) resulted, along with the glacioeustatic sealevel rise, in the rapid breakdown of the ice shield above the Barents Sea shelf (or above underwater rises, in case the continuous shield did not exist).

If this assumption is true, then sedimentation was mainly controlled by the ice rafting in combination with the influx of finely dispersed suspension from thawed water (*glacier milk*), which is reflected in the granulometric composition of sediments in the horizon III.

The transition from horizon III to horizon II is characterized by the decrease in the content of sand and

coarse silt fractions, appearance of lamination, and turbidite structures (in the eastern flank of the Central Deep). The gray, sometimes with bluish shading, coloration of the horizon III sediments is replaced in separate layers or in the entire horizon by brown color, which suggests oxidizing environments, i.e., the influx of oxygen into bottom water, and probably intermittent deceleration or complete cessation of sedimentation.

The preponderant role evidently passed from glaciomarine sedimentation to different gravity flows, whose activity was indirectly related to retreating glaciers, although the latter continued to serve as a main source of the sedimentary material. Most researchers relate the pulsating character of sedimentation, that resulted in the formation of bedded structures from turbidite cyclites to thin lamination (locally resembling varves), to the seasonal or secular variations in the intensity of the sedimentary material influx and in the activity of hydrodynamic processes. The leading role is considered to belong to flows with the elevated density at the expense of the high content of the suspended sedimentary material, that was transported by thawed water from glaciers (Korsun *et al.*, 1995; Polyak and Mikhailov, 1996; Polyak *et al.*, 1995). In opinion of Polyak with coauthors, glaciers completely retreated from the deep part of the shelf by 12.7 ka ago.

Although we generally agree with such interpretation, we should emphasize the following points. First, variations in the salinity of interstitial water (29–34‰) indicate the formation of flows from sea water. In some cases without participation of thawed water, the main volume of interstitial water probably spread over the sea surface. Second, the formation of the fresh-water surface layer prevented from vertical mixing, which resulted in, on one hand, intermittent stagnation of bottom water and favored dissolution of calcareous microfossils at the bottom (Gataullin *et al.*, 1993; Polyak and Mikhailov, 1996) and, on the other hand, suppressed biological productivity of surface water.

According to Polyak and Solheim (1994), in the Franz Victoria Trough, deglaciation occurred during a shorter period due to penetration of Atlantic water and rapid breakdown of the ice shield. However, in all other areas of the sea, this process was probably gradual (Lehman and Forman, 1992; Polyak *et al.*, 1995; Vøren *et al.*, 1988).

Freshening and low temperature of surface water hampered the development of planktonic foraminifers despite the probable brief productivity outbursts near the floating ice edge. The lower content of benthic foraminifers in deglaciation sediments is related by some researchers (Hald *et al.*, 1991) to the increase in dissolution intensity and freshening of surface water. Nonetheless, the most probable mechanism that impeded the development of the benthic foraminiferal community was very high terrigenous sedimentation rates, which is also suggested by other authors (Korsun *et al.*, 1995). Formation of sediments in marine environments is sup-

ported, in addition to the presence of foraminifers and pteropods, by the occurrence of diatoms, dwellers of the photic layer (Samoilovich *et al.*, 1993).

In the northwestern part of the sea, deglaciation terminated about 10 ka ago (Lubinskii *et al.*, 1996; Polyak and Solheim, 1994) owing to penetration of warm intermediate Atlantic water in this area along the Franz Victoria Trough. In the studied cores, evidently, the occurrence of benthic and planktonic foraminiferal species *Cassidulina teretis*, *Pullenia bulloides*, *Cibicides wuellerstorfi*, *Turborotalita quinqueloba*, and *Neoglobobulimina pachyderma* was connected with this water.

The end of deglaciation and the beginning of the Holocene stage of paleoceanographic evolution in the Barents Sea is marked in core sections by sharp changes in lithological, paleontological, and geochemical characteristics of sediments. These changes reflect the cardinal transformation of the sedimentation regime related to the establishment of paleoceanographic and paleoclimatic conditions at the boundary between glacial late Pleistocene and interglacial Holocene close to the modern environments.

The Holocene stage was characterized by cessation of the activity of dense gravity flows and by the prevalence of hemipelagic and nepheloid sedimentation. The Holocene was marked by biofiltrational precipitation of fine suspended particles throughout the entire open sea from the enriched surface water. As a result of the activity of bottom currents, this material was redistributed within the bottom nepheloid layer, i.e., washed out from underwater rises and accumulated in depressions, resulting in the thickening of the Holocene sequence by an order of magnitude and more. Proportions of the terrigenous material influx from different sources were approximately similar to those nowadays, although the role of the glacial source could be slightly higher at the beginning of the Holocene.

The Holocene stage generally differs from previous stages by the higher bioproductivity. The presence of hydrotroilite, the elevated C_{org} content (to 2.5%) and the abundance of benthic foraminifers and macrofossils indicate the high influx of planktonogenic organic matter into sediments and the development of the sulfate-reduction process. However, an intense oxidation of organic matter in bottom sediments and accumulation of carbonic acid in bottom waters throughout the entire Holocene (as well as at present) resulted in dissolution of calcareous microfossil shells. As a consequence, some layers in sections lack determinable fossil assemblages, and some cores are barren of fossils. Many researchers relate dissolution of calcium carbonate at the Barents Sea bottom to an additional influx of CO_2 and O_2 to the bottom water entering with sinking cold brine that was formed due to the freezing of surface water (Korsun *et al.*, 1994; Polyak and Mikhailov, 1996; Polyak and Solheim, 1994; Steinsund and Hald, 1994).

According to our data, sedimentation rates in the Holocene usually did not exceed 10 cm/ka as is evident from the low thickness of Holocene sediments in the flat bottom areas of the Central Deep. This is consistent with the data of Gataullin *et al.* (1993) obtained for the eastern part of the Central Deep, as well as with the isopach map of Holocene sediments compiled by Gurevich (1995). Against the background of such sedimentation rates, narrow troughs between rises are outstanding. In the latter, the thickness of Holocene sediments increases to 2–3 m and sedimentation rates of fine-grained sediments amount to 30–35 cm/ka at the expense of the bottom redistribution of the sedimentary material within the nepheloid layer. Sedimentation rates exceeding 50 cm/ka are registered in the Western Novaya Zemlya Trough (Gurevich, 1995; our data), where such high values are determined by the proximity to the provenance of fine terrigenous suspension that is transported by temporal (seasonal) flows of thawed water from glaciers and the snow cover of the Novaya Zemlya Archipelago.

The sedimentation of the early Holocene differs from that in the late Holocene in higher proportion of coarse fractions at the expense of the ice-rafted material near modern glaciers of Franz Josef Land and Severnyi Island of Novaya Zemlya. In the central part of the sea, this was provided by intense nepheloid flows that transported mainly silt from underwater rises to depressions.

The occurrence of boreal planktonic foraminifer species *Turborotalita quinqueloba* and *Neoglobobulimina pachyderma* dex. indicates an intermittent increase in the Atlantic water influx to the Barents Sea through the subsurface layer. According to some authors (Hald *et al.*, 1999; Khusid and Polyak, 1989; Polyak and Mikhailov, 1996; Polyak and Solheim, 1994), the polar form *N. pachyderma* sin., which is virtually absent in Recent sediments of the study area and in the ice-covered Arctic Ocean as a whole, is related to Atlantic water penetrating into the Barents Sea (Knies *et al.*, 1999; Nørgaard-Pedersen *et al.*, 1998). The improvement of the connection with the North Atlantic is also evident from the increased content of the Atlantic benthic foraminifer species *Cassidulina teretis* in some layers (Polyak and Mikhailov, 1996; Polyak and Solheim, 1994). The shift of the dominant role from *Cassidulina reniforme*, a species abundant in the early Holocene and connected with distal glacial biotopes and fine-grained substrates, to the group of several species such as *Buccella* spp., and low-Arctic *Islandiella helenae* and *I. norcrossi*, which are abundant in the middle Holocene, indicates reduction of the ice cover in the Arctic Ocean and increase in a seasonal productivity during that time (Polyak and Mikhailov, 1996). The abundance of *Melonis barleeanus* also increases. In the late Holocene, preponderant was a shallow-water *Elphidium clavatum*, benthic foraminiferal species characteristic of near-ice biotopes and resistant of stress conditions such as pack ice, low temperature, salinity and productivity, and high bottom hydrody-

namics (Hald and Korsun, 1997; Polyak and Solheim, 1994), which reflects cooling and growth of the ice cover in the northern areas of the sea.

The species distribution confirms previous conclusions (Polyak and Mikhailov, 1996; Polyak and Solheim, 1994) that conditions of the middle Holocene (~7–5 ka B.P., based on C isotope data) were most favorable for the development of foraminiferal assemblages, when the ice cover was reduced, whereas a seasonal productivity and Atlantic water influx increased. The rare occurrence of *Nonion labradoricum* in the middle Holocene sediments of the Perseus Trough probably indicates more northerly position of the Polar Front zone (Hald and Korsun, 1997; Polyak and Mikhailov, 1996) as compared with that in the early Holocene (Fig. 8), which was marked by the elevated content of this species. Paleooceanographic environments in the Perseus Trough, more favorable for species diversification in comparison with those in the Franz Victoria Trough, were probably related to the distant position of the former from areas of the permanent sea-ice distribution. This is evident from the higher diversity of foraminifers in Core ASV-858 as compared with that in Core ASV-880 and also from the elevated abundance of some species (for instance, *Elphidium subarcticum*) (Korsun and Hald, 1998).

Thus, the postglacial sedimentation history in the Barents Sea is generally characterized by the decreasing role of the glaciomarine sedimentation, and increasing role of processes of marine sedimentogenesis such as the lateral transport of suspension by surface and bottom currents, biofiltration precipitation of suspension controlled by biological productivity, and accumulation of planktonogenic organic matter. This was accompanied by the increase in abundance and diversity of planktonic and benthic foraminifers. Remarkable is a stage-by-stage, stepwise character of these trends related to sharp climatic and oceanographic changes.

CONCLUSION

(1) Based on lithological and micropaleontological data, three stages can be recognized in the postglacial oceanographic evolution of the Barents Sea: early deglaciation, late deglaciation, and Holocene.

(2) The early deglaciation stage (older than 13 ka in the radiocarbon scale) was characterized by the accumulation of glaciomarine sediments. Main agents of sedimentation were the influx of the fine-grained suspended material transported by thawed water from ice shields, iceberg and ice rafting, and gravity flows. The occurrence fine-grained pelite and well-preserved Recent microorganisms indicate marine sedimentation environments, whereas a gray coloration of sediments and impoverishment of fossil assemblages suggest the low bioproductivity and restricted oxygen supply of bottom waters due to the preservation of the ice cover during most of the year.

(3) The early-late deglaciation boundary (10–13 ka ago) corresponds to a sharp change in the sedimentation regime manifested in the appearance of laminated structures with alternation of brown (oxidized) and gray (reduced) laminae and turbidite interbeds. Precipitation from the repeatedly formed bottom nepheloid layers was responsible for sedimentation. Brown laminae correspond to episodes of reduced sedimentation rates or to brief breaks in sedimentation. The greater-scale ice cover of the basin and freshened, at the expense of thawed water, surface water resulted in the low bioproductivity. This assumption is supported by the rare occurrence of planktonic and benthic foraminifers.

(4) The beginning of the Holocene stage about 10 ka ago was marked by the establishment of the normal sea basin sedimentation of the hemipelagic type, the increased bioproductivity, the colonization of shelf depressions by macrobenthic communities, the enhanced early diagenetic sulfate reduction processes, and the intermittent influx of Atlantic water. The latter is evident from the abundance of Polychaeta, planktonic and, particularly, benthic foraminifers, including species connected with Atlantic waters, as well as the intensification of bioturbation upward the section and enrichment of sediments in hydrotroilite.

(5) At least three stages can be distinguished in the Holocene paleoceanographic evolution approximately corresponding to the early, middle, and late parts of this period. This is supported by the change in dominant assemblages of benthic foraminifers. The early Holocene was marked by the episodic influx of the sandy-silty ice-rafted material. The middle Holocene was characterized by the intense influx of Atlantic water, while the transition to the late Holocene, by elevated bioproductivity. In the late Holocene, the ice cover in the northern areas of the sea increased despite the intermittent penetration of Atlantic water into the Franz Victoria Trough.

The potsglacial sedimentation history from the beginning of deglaciation to the Holocene is generally characterized by the gradual decrease in the role of the glacier factor, although nowadays, the latter is particularly important in the northern areas of the sea. A rapid change in the sedimentation regime reflects short-term paleoceanographic events, whose mechanism of influence on sedimentation processes is yet to be clarified.

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Oolites of the Caspian Sea (Regularities of Distribution and Isotope-Geochemical Peculiarities)

V. Yu. Lavrushin and V. N. Kuleshov

Geological Institute (GIN), Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 109017 Russia

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Abstract—The isotope-geochemical features of carbonate oolites from recent sediments of the Caspian Sea were studied. Separate areas of their distribution were distinguished in the basin. Based on laboratory study, it was shown that recent oolites are made up of exclusively Mg-calcite differing in chemical composition. Two groups of oolites are distinguished by the degree of their magnesium content: high-Mg and low-Mg. The distribution of these groups is controlled by general hydrochemical zonality of the marine basin. The high-Mg oolite marks the recent coastal line of the eastern shore of the Southern Caspian Basin. Oolites of the second group form local accumulations in the shelf area in different parts of the basin, often coinciding spatially with oil- and gas-bearing zones, tectonic disturbances and manifestations of mud volcanism. The variations of carbon and oxygen isotopic composition in oolites are also generally controlled by isotope-geochemical characteristics of marine water and bicarbonate dissolved in it. At the same time, oolites of the Caspian Sea appreciably differ by their isotopic composition from recent carbonate fauna.

Oolites are a specific group of carbonate sedimentary formations that is widespread in recent oceanic, marine, and lacustrine sediments and in older sedimentary complexes. In this work, the term “oolites” is understood in a broad sense. This includes a wide group of “spherical or ellipsoidal mineral forms consisting of calcium carbonate, oxides of Fe and Mn, ...having a concentric-layered, sometimes radiate-fibrous structure (around the central nucleus)...” (*Geologicheskii slovar'*, 1973, p. 32).

The best-studied accumulations of recent oolites are situated in the southern part of the Persian Gulf and in the Bahamas Shoal (Pavlidis and Shcherbakov, 1995). They are also known from the western part of the Hindustan shelf (^{14}C radiometric age is 11 ka), the Sharp Bay (West Australia), and the Marmona lagoon (Baja California) (Konyukhov, 1987), and from Quaternary sediments of the Caspian Sea (Klenova *et al.*, 1956; Fedorov, 1957).

The conditions of the formation of oolites are quite similar in different areas of the Earth. They are formed on a shallow shelf or in lagoons of marine basins belonging to warm climatic zones, at depths from several meters to some tens of meters, i.e., in hydrodynamically active media oversaturated with calcium carbonate. As a rule, oolitic sand composes accumulative bodies: banks, beach barriers, etc. For instance, its maximum accumulation on the shelf of the Bahamas Shoal is observed at depths of less than 6 m; in the southern part of the Persian Gulf, oolites occur in the coastal zone and shallow shelf with a width of less than 100 km and depths of less than 45–50 m. Water temperature during the summer time reaches 32–33°C (Lyakhin, 1990).

Although voluminous data are presently available on mineralogical and chemical compositions of marine oolites (Strakhov *et al.*, 1954; Pettijohn, 1975; *Karbonaty...*, 1987; Konyukhov, 1987), the problem of their formation in marine basins is still disputable. The mechanism of the concentric layer formation is not completely clear, and irregularities of oolite distribution in sediments in basins with similar hydrochemical and hydrological conditions are not understandable. The question of the role of cyanobacterial assemblages in this process also remains controversial.

This work attempts to generalize our documentary data and the available published material on recent oolites of the Caspian Sea. Particularly significant are the data on carbon and oxygen isotopic composition that allow us to clarify some aspects of the formational conditions of oolites and the sources of their substance.

SEDIMENTATION FEATURES IN THE CASPIAN SEA DURING THE QUATERNARY

The Caspian Sea Basin is divided geographically into northern, middle, and southern parts. Tectonically, it is located within three structures of the first order. The northern and northeastern parts of the Northern Caspian Basin are situated on the Precambrian Russian Platform. The Middle Caspian Basin lies completely on the epi-Paleozoic basement of the Scythian–Turanian Plate, and the Southern Caspian Basin occupies the area within the Alpine folded belt (Lebedev *et al.*, 1973).

The Caspian Basin accumulates sediments supplied from the southeastern part of the East European Platform, as well as from slopes of mountain systems bor-

dering the sea: the Greater and Lesser Caucasus, the Lesser Balkhan, and the Kopetdag Mountain. This results in the formation of a thick sedimentary cover, up to 10 km thick in the northern part of the basin and about 24 km thick in the southern part. Enormous reserves of hydrocarbons accumulated in this thick sedimentary sequence.

The Caspian Sea is a closed drainage basin fed by large rivers, such as the Volga, Ural, Terek, Kuma, and Kura. Therefore, the position of its level is largely defined by the ratio of volumes of river discharge and evaporation from its surface, i.e., by climatic conditions in the Caspian Basin and in the adjacent areas (mainly in the Volga River basin). During the Quaternary, due to numerous climatic variations, this ratio repeatedly changed, resulting in significant sealevel fluctuations (with an amplitude of up to 50 m) (Sedletskii and Baikov, 1997) and frequent redeposition of old sediments (Varushchenko *et al.*, 1987). In warm climatic periods, carbonates, including oolitic sand, intensively precipitated from marine water. According to some authors, the sealevel fluctuations sometimes could be a consequence of vertical and lateral tectonic movements; i.e., they had a geological nature (Antipov *et al.*, 1996). Such tectonic activation had to be accompanied by the corresponding activation of hydrological regime of groundwater and, as a consequence, by the increase of the volume of subaqueous discharge.

Thus, due to different geotectonic, climatic, and hydrological conditions in the Caspian Basin, almost the whole variety of sedimentary lithogenesis typical of marine basins in warm climatic zones was realized. With the Caspian Sea, for example, one can observe peculiarities of carbonate sedimentation in zones of marine and river water mixing (the Northern Caspian Basin) and on tidal flats, similar to sabkhas of the Red Sea (the northeastern coast); one can also estimate the influence on these processes due to some local factors (for instance, subaqueous discharge of groundwater, including mud volcanism). From this standpoint, the Caspian Basin is practically an ideal object for study of conditions of carbonate sedimentation, including oolitic sand formation.

Oolitic sand in the Caspian Sea is often cemented by carbonate material. Supposedly (Klenova *et al.*, 1956, 1962), these phenomena are genetically related to each other. The cementation of sandy sediment is considered to be an early diagenetic process, while oolites are viewed as sedimentary-diagenetic formations (Bruevich *et al.*, 1946). According to some authors (Bruevich *et al.*, 1946; Klenova *et al.*, 1956, 1962), oolites are formed as a result of precipitation of calcium carbonate on sand particles suspended in marine water. Cementation of sandy sediment is noted in a chemically similar environment, but under quieter hydrodynamic conditions, under which the upper layers of sediment are not agitated. However, the works carried out on hydrochemistry of pore waters, geochemistry and lithology of

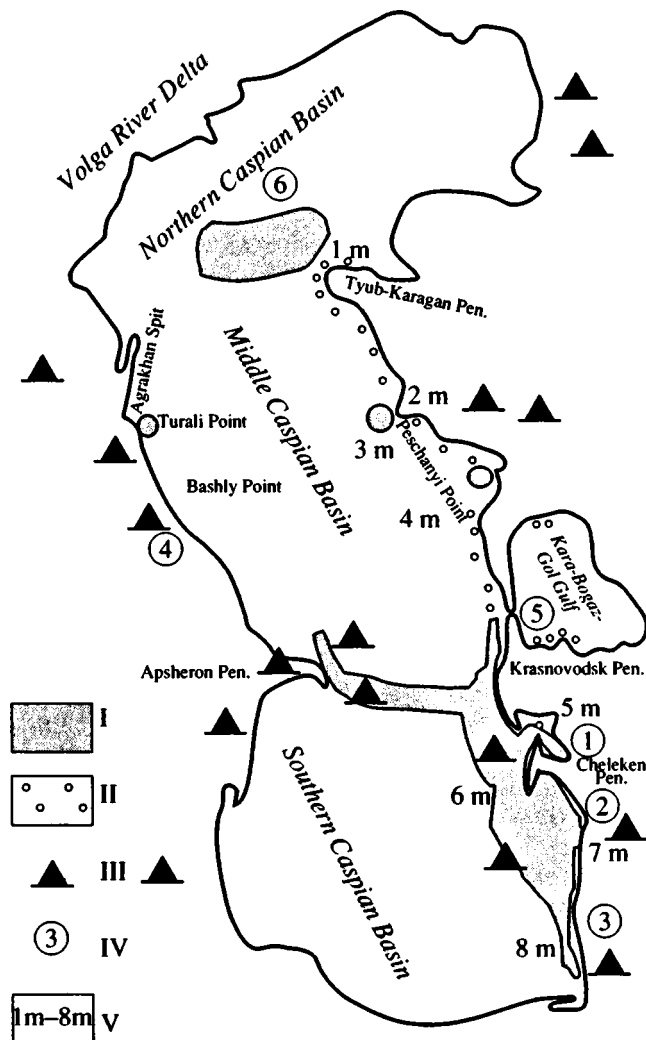


Fig. 1. Schematic distribution of oolitic sand in sediments of the recent Caspian Sea Basin, with regard to data of Klenova *et al.* (1956, 1962) and Kholodov *et al.* (1989). (I) Fields of oolite sand in original position; (II) areas of oolites redeposited from older rocks; (III) oil and gas fields; (IV) studied areas (encircled numbers): (1) northern and southern Cheleken gulfs, (2) Uzunada Gulf, (3) Okarem Settlement, (4) Adzhi Channel, (5) Spit of Kara-Bogaz-Gol Gulf, (6) Northern Caspian Basin; (V) sites of marine water sampling (Table 2).

beach sediments of the Caspian Sea, and bottom sediments of the Northern Caspian Basin allow us to have a new look at the problem of formation and genesis of oolites, as well as crusts of carbonate cementation.

MATERIALS AND RESEARCH METHODS

Coastal sediments from different seashore areas were sampled: in the east, from Bekdash Settlement to Turkmen-Bashi (on the spit of the Kara-Bogaz-Gol Bay) and from Cheleken Peninsula to Gasan-Kuli Settlement; in the west, on the Agrakhan Spit, from Caspiisk to Manas Settlement, and in the Berikei Settlement area (the Bashly Point) (Fig. 1). The chemical compo-

sition of groundwater in the coastal zone was studied in the same areas. We also examined samples of bottom surface sediments (250 samples) from the Caspian Sea presented by S.A. Brusilovskii. Previously published data by Klenova *et al.* (1956), Shul'ts (1962), and Sorokin *et al.* (1987) are also used in the work.

Transparent thin sections were prepared from sediment specimens, and morphologic features of oolites contained in them were studied (the presence of concentric layers, crystallization pattern of carbonates, type of the central zone, degree of preservation of oolites, etc.). The percentage content of oolites versus the general content of sand grains (excluding, as a rule, faunal fragments) was also calculated in thin sections.

The important problem was establishing the age of oolitic sand: whether they are recent or old, redeposited. The possibility of the presence of ancient oolites in Recent sediments is extremely high, because rocks of the Upper Jurassic, Lower Cretaceous, and Meotian are exposed along the periphery of the basin; they contain oolitic limestone and sandstone. In the Lower Quaternary sediments, oolites are also known in sand and limestone of Baku and Khazar ages on the eastern coast, in the area of Krasnovodsk and Cheleken peninsulas (Fedorov, 1957).

Unfortunately, there are few radiocarbon and faunal datings of oolitic sand, and in the works, where these data are presented, the features of lithological composition of the marine sediments, as a rule, are not properly described. We obtained a radiocarbon dating of oolitic sand from the southeastern coast (the Usunada Bay south of Cheleken Peninsula). The $\delta^{14}\text{C}$ age of this sand is 7080 ± 450 yr (Sample GIN-6206; determination by L.D. Sulerzhitskii; the sand sample was taken from the surface of a coastal barkhan). Fragments of ancient carbonate rocks were also present in the sample with the ooids. Therefore, one can assume that the ooids from the southeastern coast may be significantly younger. A number of observations agree with this; among other things, we noted that the coating of terrigenous particles by carbonates continues to this day.

It should be recognized that, in most cases, we are not able to confidently define the age of oolites. However, their morphological characteristics revealed under the microscope offer a view of oolites in original position or redeposited from older sediments.

The criterion of their *in situ* occurrence can be the degree of preservation and the percentage content in sediment. Under conditions of a shallow-water basin, carbonates are intensively abraded; hence, the redeposited oolites must be distinguished by poor preservation of concentric layers. In such a case, their sediment concentration also decreases because of their dilution with recent terrigenous material (content of such oolites in sediment rarely exceeds 3–5% of sand grains). Ancient oolites are characterized also by a high degree of crystallization of carbonate concentric layers; they are made up of large isomorphic crystals of calcite or have

radiate-fibrous interior structure. Recent oolites more often consist of micritic carbonate (Figs. 2a, 2b).

Thus, one can determine when oolites are in the original occurrence. However, the problem still remains unsolved: is their formation currently in progress, or is their presence in Recent sediments related to abrasional exposure of older deposits? Some additional information on these questions sometimes comes from the examination of faunal fragments in thin sections. The coating of fresh faunal remains with carbonates may testify to the recent origin of oolites. Conversely, an admixture of shell fragments, without signs of coating with secondary minerals, may be evidence for the origin of oolites from old sediments stripped, for example, by recent erosion.

The chemical composition of carbonates from oolites was determined in a Camebax X-ray microanalyzer (Table 1). The chemical analysis of pore water was carried out in the field (for unstable components) and in laboratory. The results are shown in Table 2.

For the isotopic investigation, samples of sand sediment were sieved in order to separate fragments of fauna and thin carbonate detritus. However, it should be recognized that such preparation of the samples does not allow fine faunal and carbonate particles to be completely removed. Afterwards, the chosen samples were treated with orthophosphoric acid (H_3PO_4) at room temperature during 1 h, using a standard technique (McCrea, 1950). The isotopic composition was determined in a MI-1201B mass-spectrometer. The obtained values during the experiments, carried out in parallel, coincided within $\sim 0.25\%$. The results are presented in Table 3.

OOLITES IN QUATERNARY SEDIMENTS OF THE CASPIAN SEA

In sediments of the Caspian Sea, oolitic sand and carbonate cementation are most often encountered in sediments of the Neocaspian age. On the eastern shelf, they were observed at the base of the Neocaspian beds discordantly overlying the sediments of the Mangyshlak regression (Klenova *et al.*, 1956, 1962). In the area south of Cheleken Peninsula, light gray oolitic sand form barkhans, beach-ridges, and beaches, desiccated after 1930.

In older sediments, oolites are found at the base of sand banks of Khazar age on the eastern coast of the sea (Fedorov, 1957). For example, in sands of the southern Cheleken sand bank, we noted old (possibly Khazar) oolites. The oolites, with small round fragments of fauna, are colored in yellow and red-brown tints. With the diameter of 1.0–1.5 mm, they are evidently distinguished by a low density; therefore, their accumulation takes place on the top of sand bars separating channels and lagoons. This is probably conditioned by peculiarities of their inner structure; the radiate-fibrous layers are micritized and partially decompacted (Fig. 2b). The

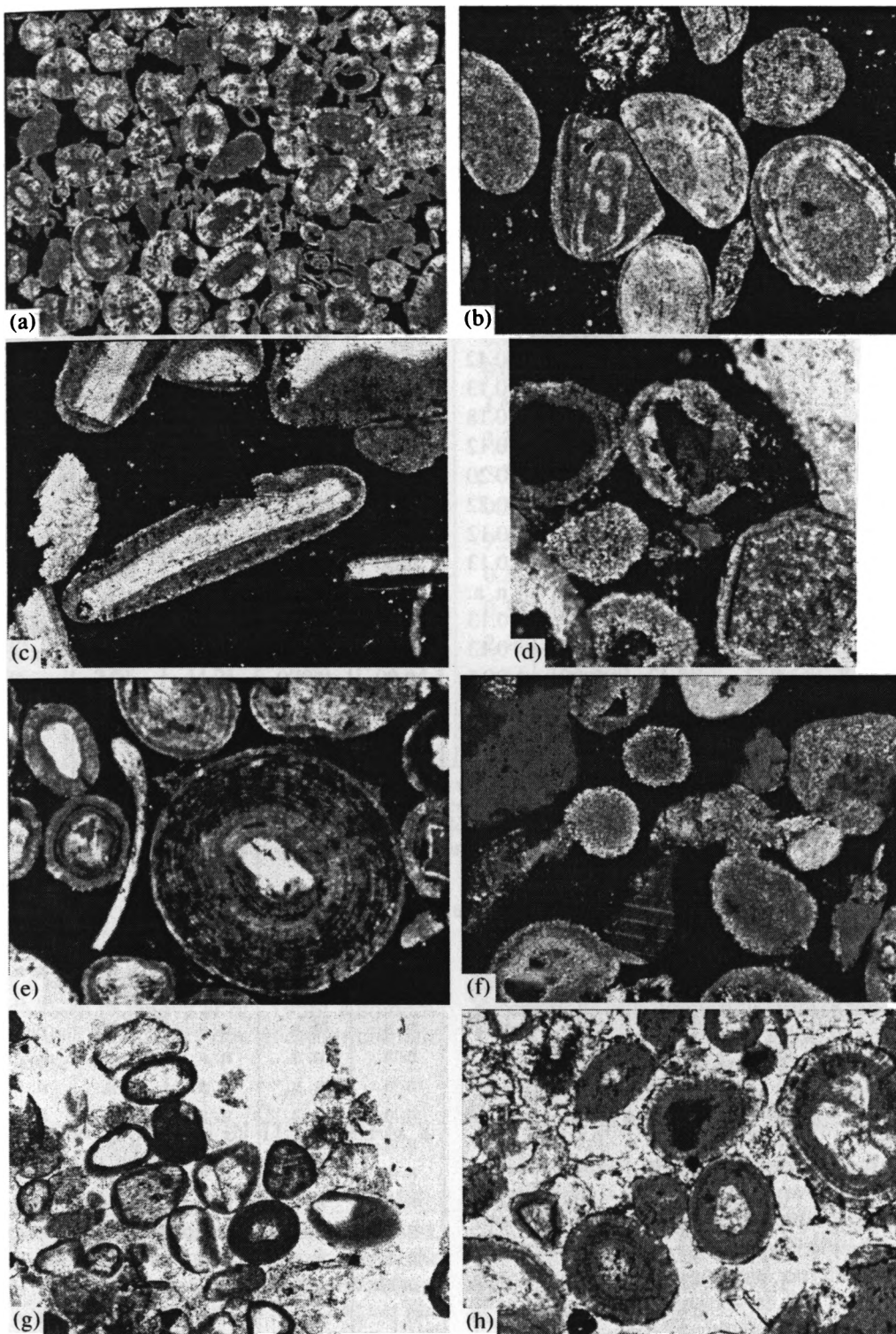


Fig. 2. Photomicrographs of transparent thin sections of oolites from the Caspian Sea. Ancient oolites: (a) Meotian oolitic limestone (Mangyshlak Peninsula), (b) redeposited oolites from the southern Cheleken Spit (Khazar?); Recent oolites: (c) accretion of micritic carbonate to faunal fragments (Northern Caspian Basin, Fig. 3, sample 23); (d) accretion of micritic carbonate to sand particles (Northern Caspian Basin, Fig. 3, sample 25); (e) oolites from the Northern Caspian Basin (Fig. 3, sample 13); (f) bloblike carbonate aggregates (southeastern coast of the Southern Caspian Basin); (g) accretion of high-Mg micritic calcite to silicate particles (southeastern coast of the Southern Caspian Basin, Uzunada Gulf, area 2 in Fig. 1); (h) oolites from mud volcanism area (southeastern coast of the Southern Caspian Basin, Okarem Settlement, area 3 in Fig. 1). (a–f) Crossed nicols, (g, h) parallel nicols.

Table 1. Chemical composition of oolites from the Caspian Sea, wt %

No. in Fig. 1	Sample no.	MgO	CaO	MnO	FeO	SiO ₂	Al ₂ O ₃	Na ₂ O	P ₂ O ₅	SO ₄	Mg mol %
Southeastern coast of the Southern Caspian Basin											
1	71	4.51	49.06	0.02	0.09	0.08	n. a.	0.18	n. a.	0.42	11.35
1	71	4.10	49.52	0.02	0.66	0.65	n. a.	0.22	n. a.	0.43	10.34
1	71	4.26	49.69	0.04	0.60	0.67	n. a.	0.14	n. a.	0.45	10.65
1	71	4.67	50.09	0.05	0.16	0.32	n. a.	0.2	n. a.	0.57	11.49
2	33/90	4.62	50.89	0.00	0.15	0.00	n. a.	0.28	n. a.	0.07	11.22
2	33/90 cr	4.86	48.58	0.03	0.21	0.00	n. a.	0.22	n. a.	0.45	12.21
2	32/90	2.99	46.51	0.32	3.17	3.96	n. a.	0.26	n. a.	0.43	8.21
2	32/90	2.68	43.63	0.14	6.14	3.34	n. a.	0.29	n. a.	0.33	7.87
2	103	4.33	47.95	0.07	0.42	2.35	n. a.	0.33	n. a.	0.41	11.17
2	206a c. z.	1.75	47.69	0.00	0.13	0.13	0.340	n. a.	n. a.	n. a.	4.85
2	206a c. l.	4.37	43.17	0.01	0.18	0.76	0.200	n. a.	n. a.	n. a.	12.34
2	1b	5.38	51.47	0.00	0.12	0.00	0.000	n. a.	n. a.	n. a.	12.69
2	1b	4.96	47.3	0.00	0.20	0.00	0.000	n. a.	n. a.	n. a.	12.73
2	207c	4.89	49.88	0.00	0.22	0.00	0.000	n. a.	n. a.	n. a.	12
2	207c	4.49	52.95	0.00	0.12	0.00	0.000	n. a.	n. a.	n. a.	10.55
2	208c	3.45	51	0.00	0.13	0.00	0.000	n. a.	n. a.	n. a.	8.6
2	103c	5.42	52.59	0.23	n. a.	0.00	0.000	n. a.	n. a.	n. a.	12.53
2	5/86 c	4.60	49.79	0.00	0.13	0.10	0.010	n. a.	n. a.	n. a.	11.38
2	3d c. z.	0.81	48.59	0.00	0.13	0.00	0.000	n. a.	n. a.	n. a.	2.26
2	3d c. l.	4.72	46.42	0.00	0.16	0.00	0.000	n. a.	n. a.	n. a.	12.39
2	5/86 c. z.	0.39	47	0.00	0.06	0.00	0.000	n. a.	n. a.	n. a.	1.14
2	5/86 c. l.	4.75	47.07	0.00	0.42	0.00	0.000	n. a.	n. a.	n. a.	12.31
2	206d	4.02	46.28	0.00	0.15	0.42	0.140	n. a.	n. a.	n. a.	10.78
2	4-1	5.50	49.53	0.00	0.00	0.04	0.000	n. a.	n. a.	n. a.	13.38
2	4-1 cr	4.87	51.48	0.04	0.00	0.32	0.000	n. a.	n. a.	n. a.	11.62
3	123	4.04	50.98	0.08	0.66	1.77	n. a.	0.22	n. a.	n. a.	9.93
3	123	4.09	48.75	0.01	2.71	1.71	n. a.	0.28	n. a.	0.46	10.45
Western coast of the Middle Caspian Basin (Dagestan)											
4	4-5	3.58	46.75	0.07	1.39	n. a.	n. a.	n. a.	n. a.	n. a.	9.62
4	4-5	1.75	47.36	0.12	2.32	n. a.	n. a.	n. a.	n. a.	n. a.	4.88
4	4-5	3.47	47.93	0.16	0.19	n. a.	n. a.	n. a.	n. a.	n. a.	9.14
4	4-3 c. z.	2.33	41.73	0.13	0.20	n. a.	n. a.	n. a.	n. a.	n. a.	7.2
4	4-3 c. l.	3.22	45.21	0.00	0.03	n. a.	n. a.	n. a.	n. a.	n. a.	9.01
4	4-2	2.79	41.54	0.14	1.12	n. a.	n. a.	n. a.	n. a.	n. a.	8.54
4	4-1 c. z.	0.70	47.64	0.13	0.00	n. a.	n. a.	n. a.	n. a.	n. a.	2.0
4	4-1 c. l.	2.18	36.76	0.10	2.87	n. a.	n. a.	n. a.	n. a.	n. a.	7.62
4	4-1 c. z.	3.37	48.17	0.30	0.06	n. a.	n. a.	n. a.	n. a.	n. a.	8.86
4	4-1 c. l.	0.05	50.13	0.09	0.03	n. a.	n. a.	n. a.	n. a.	n. a.	0.13
4	4-1 c. z.	1.50	35.09	0.19	2.05	n. a.	n. a.	n. a.	n. a.	n. a.	5.61
4	4-1 c. l.	2.41	43.87	0.12	0.67	n. a.	n. a.	n. a.	n. a.	n. a.	7.09
4	4-1	1.39	37.94	0.12	2.06	0.79	n. a.	n. a.	n. a.	n. a.	4.84
4	4-1	2.18	45.34	0.15	0.25	0.17	n. a.	n. a.	n. a.	n. a.	6.26
4	1	3.77	46.34	0.19	2.47	1.14	n. a.	n. a.	n. a.	n. a.	10.16
4	1	3.90	49.78	0.12	1.92	0.42	n. a.	n. a.	n. a.	n. a.	9.82
4	1	2.69	48.28	0.62	1.74	0.34	n. a.	n. a.	n. a.	n. a.	7.19
4	1	1.61	48.16	0.34	2.15	1.95	n. a.	n. a.	n. a.	n. a.	4.44
4	1	2.44	49.04	0.11	2.61	0.83	n. a.	n. a.	n. a.	n. a.	6.47
4	1	2.62	52.89	0.05	2.85	0.45	n. a.	n. a.	n. a.	n. a.	6.44
8	70*	2.57	39.16	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	8.37
8	125*	2.59	49.61	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	6.77

Table 1. (Contd.)

No. in Fig. 1	Sample no.	MgO	CaO	MnO	FeO	SiO ₂	Al ₂ O ₃	Na ₂ O	P ₂ O ₅	SO ₄	Mg mol %
Spit of the Kara-Bogaz-Gol Gulf											
5	K3	1.27	51.62	0.00	0.04	0.21	0.000	0.09	0.644	n. a.	3.31
5	K3	1.00	54.01	0.00	0.04	0.00	0.000	0.00	0.755	n. a.	2.5
Water area of the Northern Caspian Basin											
6	33	3.04	51.21	0.25	2.04	3.92	1.806	n. a.	n. a.	n. a.	7.64
6	33	2.70	47.55	0.06	2.88	1.59	0.786	n. a.	n. a.	n. a.	7.52
6	33	2.38	44.03	0.09	2.80	0.74	0.653	n. a.	n. a.	n. a.	7.01
6	33	3.04	57.99	0.06	3.54	0.00	0.000	n. a.	n. a.	n. a.	6.81
6	33	3.09	50.07	0.25	2.53	1.63	0.088	n. a.	n. a.	n. a.	7.91
6	33	3.37	42.16	0.36	7.46	3.34	1.012	n. a.	n. a.	n. a.	10.01
6	223	2.04	45.05	0.00	2.95	3.73	0.000	0.2	0.769	n. a.	5.93
6	223	3.27	48.81	0.00	0.95	0.30	0.000	0.12	0.904	n. a.	8.54
6	224	2.49	39.91	0.00	0.28	9.32	0.000	0.48	0.45	n. a.	7.98
6	231	1.89	52.42	0.00	1.15	0.21	0.000	0.15	0.763	n. a.	4.79
6	231	2.95	48.47	0.00	1.14	0.37	0.000	0.16	0.543	n. a.	7.82
6	236	1.04	51.6	0.00	2.72	2.44	0.000	0.14	0.722	n. a.	2.73
6	236	2.95	44.01	0.00	1.44	2.64	0.000	0.13	0.644	n. a.	8.54
6	163*	2.98	49.86	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	7.68
6	726*	6.22	46.04	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	15.8

Note: Analyses were performed in a Camebax microanalyzer. Analyses of samples 70, 123, 163, and 726 are adopted from (Shul'ts, 1962). Monotype numbers in column 2 correspond to different oolites from the same sample; (c. z.) central zone of oolite (nucleus); (c. l.) concentric layers (if chemical determination was carried out for one oolite). (a, b, c) Sampling depth (50, 100, and 250 cm, respectively, from sediment surface). (cr) carbonate cementation crust. (n. a.) not analyzed.

reddish tint is possible evidence that their initial composition included Fe²⁺ that was oxidized with time.

Authigenous oolites in late and early Khvalyn sediments are not known (Klenova *et al.*, 1956; Kholodov *et al.*, 1989). This is most likely due to colder climatic conditions of those periods.

DISTRIBUTION OF OOLITES IN THE SURFACE SEDIMENTS

General Regularities of Distribution over the Basin

In the Holocene sediments of the southeastern coast, oolites in original position are not found above the absolute level of -20.4 m, i.e., above the maximum level of the Neocaspian transgression (5-6 ka ago). The latter stood about 6 m higher than the sealevel in 1978 (Fedorov, 1980; Varushchenko *et al.*, 1987). They are encountered on the shelf to the water depths of 35-50 m (Leont'ev, 1957; Rychagov, 1974; Sorokin *et al.*, 1987).

Oolites are most widespread on the shelf near the eastern coast, in the area of the Mangyshlak Sill, within the Baku Archipelago, and in some places of the Dagestan shelf (Fig. 1). The microscopic investigations

suggest that the major part of oolites from the eastern coast (from Krasnovodsk Peninsula to Mangyshlak Peninsula) is likely to have a clastic origin. The detailed descriptions of bottom sediments (Klenova *et al.*, 1956, 1962), as well as our data, made it possible to distinguish the sections with original occurrence of oolites in this region. They occupy a significantly lesser space than formerly recognized (Fig. 1).

Other areas of oolitic sand occurring *in situ* were revealed in a similar way. It was found that they are most widespread on the shelf adjacent to the southeastern coast (south of Cheleken Peninsula), in the area of the Baku Archipelago, and on the Mangyshlak Sill (Fig. 1). In other places of the western and eastern coasts of the Middle Caspian Basin, oolites form local accumulations at depths of 8-12 m in the areas of the Turali Lake and Bashly (Berikei) Point in Dagestan, as well as abeam with the spit of the Kara-Bogaz-Gol Bay, Fetisovo Settlement, and Peschanyi Point. The occurrence of oolitic sand is related, as a rule, to small elevations (Klenova *et al.*, 1956, 1962). Here, the oolite content in sand fraction reaches 70-80% and higher. In sediments from adjacent areas, they are present in the

Table 2. Chemical composition of pore and marine waters from the Caspian Sea (concentrations in mg/l)

Ord. no.	Sample no. and location	pH	Eh	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	SiO ₂	H ₂ S	Dry residue
Pore water in sediments from the southeastern coast, the Uzunada Gulf (no. 2 in Fig. 1)													
1	1a	7.16	71	9500	345	356	1665	584	17020	5380	61.5	0.0	36.3
2	1b	7.04	-100	26650	750	505	5690	341	47516	17452	59.5	0.0	102.12
3	1c	7.15	-112	38450	1100	541	8110	353	67374	24802	58.0	0.0	142.02
3	1d	6.71	-146	46000	1233	577	9411	439	84749	28642	42.0	0.0	172.1
4	1e	6.52	-168	44225	1133	621	8925	768	82267	25544	50.0	20.4	169.12
5	1f	6.78	-188	40375	950	641	8390	951	75175	23615	51.0	22.8	157.24
6	205a	7.55	120	9275	375	392	2152	427	17730	7210	53.0	13.9	41.52
7	205b	7.35	-90	19075	558	537	4170	378	34041	13942	61.0	3.4	78.64
8	205c	7.13	-110	26650	705	589	6080	439	47516	19586	58.5	3.4	109.24
9	205d	7.07	-103	35750	1000	541	7052	481	60991	21218	50.0	0.0	124.24
10	205e	6.98	-100	35750	727	561	7685	634	61700	21044	50.5	21.4	130.02
11	205f	6.93	-204	25825	556	529	5715	725	46098	15466	47.5	46.2	98.34
12	1r-a	7.25	-121	10900	345	617	3064	786	19148	11074	62.5	12.6	49.62
13	1r-b	6.71	-135	16350	458	713	3939	805	29077	13521	60.0	25.5	69.14
14	1r-c	6.87	-142	16350	444	673	4268	878	33332	13225	70.0	80.0	74.86
15	1r-d	6.84	-151	18175	360	488	4170	1403	34041	10942	60.0	102.0	73.4
16	1r-e	6.73	-322	17000	331	480	4158	1531	32977	10217	63.5	115.3	72.66
Marine water near the eastern coast of the Caspian Sea (nos. 1m-8m in Fig. 10)													
17	Bautino	8.22	360	3480	164	320	717	192	5296	3600	1.6	0.0	14.07
18	Ashi-Sor	8.29	350	9475	500	920	2223	195	16392	9936	11.5	0.0	41.05
19	Peschanyi Point	8.28	375	3240	164	300	778	229	5296	3792	1.9	0.0	14.06
20	Bekdash	8.31	405	3400	164	300	741	229	5674	3408	10.5	0.0	14.08
21	Northern Cheleken Gulf	8.35	320	5672	234	460	1118	155	8196	5520	1.8	0.0	21.5
22	Southern Cheleken Gulf	8.45	360	4300	200	400	863	177	6935	4368	37.5	0.0	16.7
23	Usun-Ada Gulf	8.37	370	3500	174	340	875	201	7092	3493	0.8	0.0	16.24
24	Okarem	8.24	380	3500	169	336	814	213	6737	3526	17.2	0.0	16.44
Pore water in sediments of the southern Cheleken Spit (no. 1 in Fig. 1)													
25	20a spit base	6.96	355	2624	128	840	413	372	5043	3360	32.0	0.0	13.06
26	20b Aladzha Settlement	7.25	335	3175	150	460	729	1159	5296	3936	65.0	0.0	14.82
27	20c	7.3	140	4517	180	220	1106	2007	8196	3456	50.0	0.0	19.94
28	20d	7.3	251	4448	172	140	972	1854	8196	2736	57.5	0.0	18.5
29	21b	7.33	365	8555	385	600	644	344	14501	7200	47.5	0.0	36.98
30	21c-d	6.99	285	10805	372	660	1786	1564	20175	5136	52.0	0.0	47.5
31	50a southern termination of the spit	7.44	195	3800	164	520	765	290	6305	4272	13.8	0.0	16.04
32	50b	7.43	280	6537	304	180	1337	888	9079	5712	23.8	0.0	22.96
Pore water in sediments of the northern Cheleken Gulf (no. 1 in Fig. 1)													
33	37b	6.69	125	33750	915	1180	5674	213	66200	7872	19.0	0.0	126.48
Pore water in sediments of the southern Cheleken Gulf, the neck of Cheleken Peninsula (no. 1 in Fig. 1)													
34	42a	7.56	366	15780	750	660	3499	271	26480	12912	17.0	0.0	64.38
35	42b	7.19	310	31450	1250	520	6901	350	52330	22032	14.5	0.0	124.2
36	42c	7.05	110	26612	1250	520	6148	375	46025	19536	32.5	0.0	107.61
37	42d	6.68	330	29838	1250	600	6561	320	51952	21072	22.5	0.0	120.03
38	42e	6.88	133	32263	1562	520	6901	338	53591	22512	26.0	0.0	123.56
39	42f	6.85	160	28625	1250	540	6136	372	46655	19776	37.5	0.0	112.4
Thermal water from springs in the Berikei Settlement area (Bashly Point, Dagestan, no. 4 in Fig. 1)													
40	Adzhi Channel, a spring	6.75	n. a.	16500	630	180	85	1610	50410	1780	44.5	21.25	n. a.
41	Berikei, a well	6.45	n. a.	26660	888	1263	377	1171	74130	1920	36.0	0.0	n. a.

Note: (a, b, c, d, e, and f) sampling depth 50, 100, 150, 200, 250, and 300 cm, respectively; (n. a.) not analyzed.

Table 3. Isotopic composition of carbon and oxygen in oolites from the Caspian Sea

No. in Figs. 1 and 3	Sample no.	Sediment sampling depth	$\delta^{13}\text{C}$ PDB, ‰	$\delta^{18}\text{O}$ SMOW, ‰	Oolites in sand (%)	Sample description
Southern Caspian, the southeastern coast						
<i>Usunada Gulf</i>						
2	3/86	0	2.3	27.2	75	Coastal barkhan, oolitic sand ("White Sand"—Neocaspian)
2	3.m	0	2.9	29.0	25	Fine-dispersed carbonate from lagoon (detritus) with gypsum segregations
2	4-1/86	0.1	-0.4	29.5	100	Carbonate cementation crust of oolitic sand
2	1a	0.5	2.6	28.7	75	Oolitic sand of a beach-lagoon zone (Neocaspian)
2	1b	1	2.3	28.0	60	"
2	103a	0.5	2.2	27.7	80	"
2	103b	1	2.1	27.6	60	"
2	207a	0.5	2.2	27.6	75	"
2	207b	0.1	2.2	27.6	70	"
2	1103	0	2.6	28.3	50	Calcareous mud (detritus) from sediments of a gulf (Neocaspian; water depth 4.5 m; distance from the shore 4 km)
2	-	0	0.8	22.4	0	"Red" carbonate sand (without oolites), the surface of a barkhan (possibly, the early Khvalyn)
2	4-4	0	1.5	29.7	0	Recent fauna (Dreisena), beach zone
2	4-4	0	1.8	30.2	0	Recent fauna (<i>Kardium edule</i> L.), beach zone
<i>Northern Cheleken Gulf</i>						
1	72/90(1)	0	1.3	27.1	80	Oolitic sand from coastal bakhans (Khazar?)
1	72/90(2)	0	2.2	27.9	80	"
1	33/90	0.15	3.0	30.3	100	Cemented oolitic sand from a mineral water vent (Neocaspian)
Western coast of the Middle Caspian Basin, Dagestan, the channel issued from the Adzhi Lake						
4	120/90	0.4	0.9	28.1	90	Cemented oolitic sand (Neocaspian)
4	135/90	4	10.5	28.9	0	Travertine
Northern Caspian water area						
<i>Northern Zone</i>						
8	317/25	0	-2.9	22.0	0	Sand fraction of calcareous mud
9	339/45	0	-1.7	25.1	0	"
10	344/50	0	-1.4	24.3	0	"
11	36	0	-3.9	21.8	1	"
12	5a	0	-2.1	22.8	0	"
<i>Main field of oolitic sand</i>						
13	33	0	2.1	26.7	79.6	Oolitic sand (bulk composition), calcite fraction
13	33	0	3.0	24.9	79.6	dolomite fraction
13	33	0	1.2	27.0	95	low-magnetic fraction of oolites
13	33	0	1.7	27.6	95	high-magnetic fraction of oolites
14	34	0	-0.8	25.7	8.6	Sand fraction of oolitic sand
15	32	0	0.5	26.3	25	"
16	236	0	-0.5	25.4	5	"
17	238	0	0.2	22.5	17.4	"
18	239	0	-0.8	25.5	3.6	"
19	279	0	-0.5	25.8	0	"

Table 3. (Contd.)

No. in Figs. 1 and 3	Sample no.	Sediment sampling depth	$\delta^{13}\text{C}$ PDB, ‰	$\delta^{18}\text{O}$ SMOW, ‰	Oolites in sand (%)	Sample description
20	280	0	0.2	26.3	17	Sand fraction of oolitic sand
13	33	0	-2.1	25.5	0	Recent fauna (<i>Kardium edule</i> l.)
13	33	0	-1.0	24.4	0	Recent fauna (<i>Kardium edule</i> l.)
<i>Central zone</i>						
21	281	0	0.9	26.6	25	Central zone
22	283	0	0.4	26.3	1	"
23	284	0	0.8	27.2	80	"
24	285	0	0.9	27.6	20	"
24	285	0	-0.2	25.9	0	Recent fauna (<i>Kardium edule</i> l.)
<i>Southwestern zone</i>						
25	21	0	1.3	20.0	26	Sand fraction of oolitic sand
26	223	0	1.2	29.5	10	"
27	224	0	0.3	26.0	11	"
28	288	0	3.5	29.5	20	"
25	21	0	0.8	29.1	0	Recent fauna (<i>Kardium edule</i> l.)
25	21	0	0.7	30.0	0	Recent fauna (<i>Kardium edule</i> l.)
<i>Southeastern coast of the Northern Caspian Basin, coastal zone of the Tyub-Karagan Peninsula</i>						
29	231	0	1.3	29.2	10	Sand fraction of oolitic sand
30	30	0	-7.6	12.4	4.2	"
31	31	0	0.0	26.2	20.3	"

form of admixture up to 5–10% (more frequently 0.5–1%) of sand grains.

Distribution of oolites in sediments of the Northern Caspian Basin

The regularities of oolite distribution in the recent seafloor sediments and their morphological types were studied in the Northern Caspian Basin. According to morphological signs, most of the oolitic sand are syngenetic with the host sediments. The oolite content varies from 0 to 80%. Maximum concentrations (around 80%) are observed only at two sites surrounded by vast aureoles (Fig. 3). Thus, there is an impression that oolites in the Northern Caspian Basin were formed only in local zones. In a spatial aspect, they are located on sand banks situated at the boundary between the Northern and Middle Caspian basins, which correspond approximately to the Mangyshlak Sill. Here, the water depth does not exceed 10 m.

Oolites of the Northern Caspian Basin are noted for high variability of morphological types. In the western and central parts of the Mangyshlak Sill, concentric layers of oolites are made up of micritic calcite (Zhemchuzhnaya and Rakushechnaya banks) (Figs. 2c, 2d). Faunal fragments or sand grains serve as the centers of their crystallization. Accretion of fauna seems to indicate the recent origin of these sands.

Eastward, near the Kulaly Island, radiate-fibrous oolites with well-expressed concentric layers appear (Fig. 2e). Because the accretion of carbonates to shell fragments is almost not observed, one can suppose that these oolites are older than those from the western areas of the Mangyshlak Sill. It is also possible that they underwent substantial diagenetic transformations. However, their good preservation, high content in sediments (up to 80%), and a great variety (up to 17) of morphological types (Shul'ts, 1962) may suggest that the oolites are in their original position. Unlike the oolites of the western areas, their concentric layers contain iron compounds (Table 1). The surface of such grains is often covered by dark-colored hard films of oxides of Fe and Mn(?) imparting weak magnetic properties. The iron content varies in the oolites, and, evidently, it is precisely these variations that explain changes of their color from black to yellow, noted in westward direction on the Mangyshlak Sill (Kholodov *et al.*, 1989; Klenova *et al.*, 1956; Shul'ts, 1962; Shternberg *et al.*, 1975).

In sediments from the western and southwestern coast of the Kulaly Island (Tyulen'i Islands), particles with a bloblike structure without a central nucleus and concentric layers were found. Similar aggregates are often encountered also in other parts of the basin, e.g., in sediments of the Turkmeni and Dagestan coasts (Fig. 2f). They are made up of micritic carbonate. Their

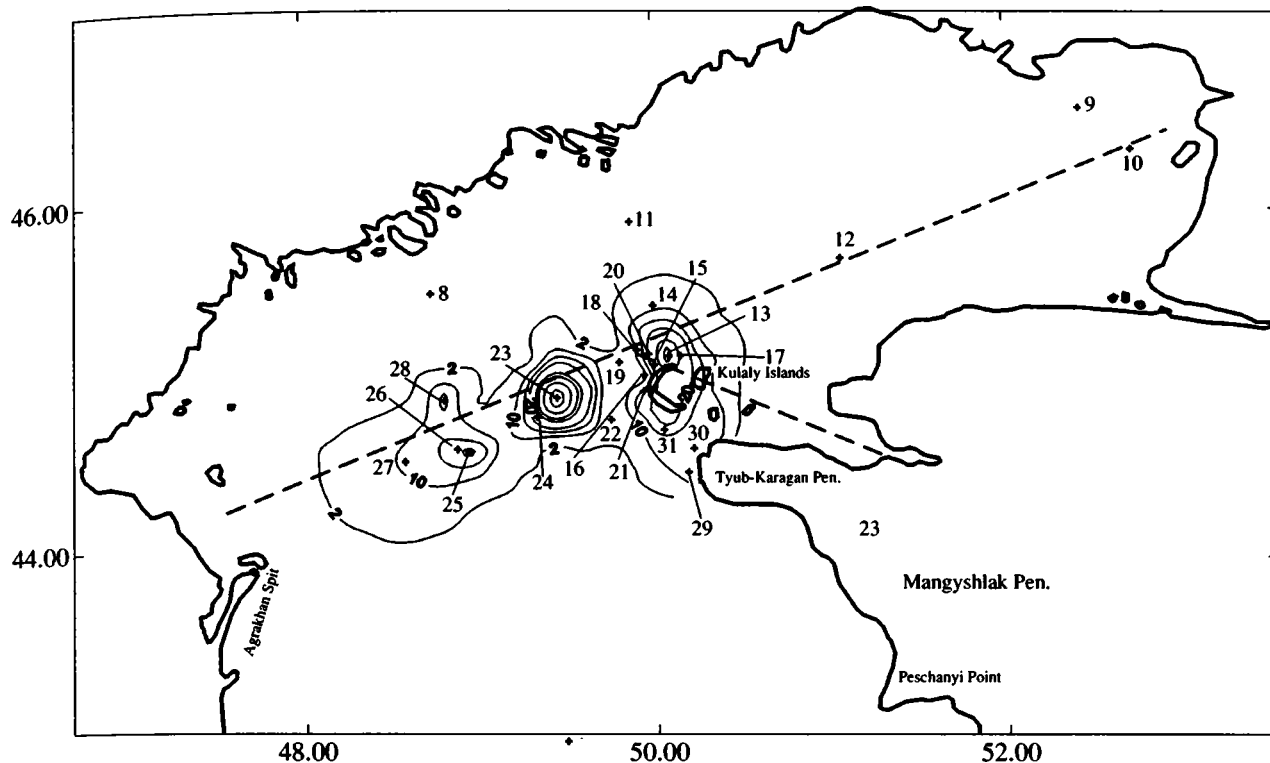


Fig. 3. Content of oolites in surface bottom sediments of the Northern Caspian. Concentration of oolites is shown by isometric lines (% of number of sand grains). Figures denote sample numbers with $\delta^{13}\text{C}$ datings (Table 3, column 1).

findings are associated with fine carbonate-terrigenous muds. Such regularities of oolite structure may be conditioned by quieter hydrodynamic conditions of sedimentation.

Eastward of the Kulaly Island (closer to the Tyub-Karagan Point), a share of old (reworked) oolites increases. At the same time, clasts of Neogene carbonate rocks appear as well.

Geological position of oolitic sand fields in the Northern Caspian Basin

The described centers of the development of oolitic sand coincide with areas of fine-dissected topography related to neotectonic movements in the Earth's crust (Lebedev *et al.*, 1973, 1975). The Malaya Zhemchuzhnaya, Srednyaya Zhemchuzhnaya, and Bol'shaya Zhemchuzhnaya shoalbanks, on top of which the maximum accumulations of oolitic sand are observed, are of tectonic origin and mark a regional, NE-trending fault zone (Leont'ev, 1957; Malovitskii, 1970) (Fig. 3). North of the Kulaly Island (where an accumulation of 'ferruginated' oolites is located), there is an intersection of two faults. Thus, a spatial linkage of the fields of oolitic sand to the areas of neotectonic activity can be noted.

This assumption conforms with V.N. Kholodov's data who pointed out a regular increase of thickness of

oolitic sand sequence on slopes of Paleogene synsedimentary folded structures in the Fergana Valley (Kholodov *et al.*, 1956).

Tectonically weak zones often serve as feeder channels for fluids coming from depth. Possibly, subaqueous discharge of groundwater is a local factor (or one among several) which causes the formation of oolites to occur only in certain localities of the Northern Caspian Basin.

It is also interesting to note that on land (on Buzachi Peninsula), manifestations of recent mud volcanism are known (Orudzheva *et al.*, 1982), and this phenomenon possibly takes place also on the eastern shelf of the Northern Caspian Basin (e.g., in the area of the Kulaly Island).

The presence of permeable zones and discharge of underground fluids in the Northern Caspian Basin confirms the data of Shul'ts (1962), who particularly pointed out the presence of bitumen in oolitic sand on the Kulaly Shoalbank. This also fits well with the data of Klenova (1956, 1962) who reported a high concentration of bitumen (0.001–0.01%) in sediments of the Ural'skaya Borozdina and the eastern part of the Mangyshlak Sill. On the Mangyshlak Sill, such anomalies correspond to cores of anticlinal folds (and in many cases to oolite accumulations).

In the Ural'skaya Borozdina, oolites are not formed, although pelletlike blobs, which consist of pelitomor-

phic calcite and are similar (in dimension) to oolites, are encountered in its central part. Evidently, the formation of oolites does not take place here because of quieter hydrodynamic conditions. In addition, this part of the Northern Caspian Basin is affected by two large rivers, the Volga and Ural; hence, marine water in this region has lower mineralization (Pakhomova and Zatuchnaya, 1966; *Kaspiiskoe more...*, 1986).

Thus, in the Northern Caspian Basin, oolitic sand fields spatially coincide with local elevations marking the deep fault. An increased bitumen content recorded within these elevations may be evidence for the discharge of deeply circulating fluids in these places.

However, it should be also taken into consideration that trends of the fields of oolitic sands in the Northern Caspian Basin coincide with the location of the "hydro-front", i.e., the boundary on which there is a mixing of mineralized water of the Middle Caspian Basin (~12 g/l) and fresh water of the Volga River (Bondarenko *et al.*, 1988). During some seasons (depending on volumes of the Volga River water delivery), water mineralization in the area of the Mangyshlak Sill can vary from n g/l to 10–12 g/l, with the front width equal to 20–40 km (Bondarenko and Zhmur, 1990). Probably, the mixing of marine and river waters may provide favorable conditions for the settling of chemogenic carbonates, but this does not explain the clearly expressed localization in the distribution of oolitic sand.

Oolitic Sand—an Indicator of Subaqueous Discharge in the Caspian Sea?

The distribution of oolitic sand fields in other parts of the Caspian Sea Basin additionally counts in favor of their relation to areas of underground fluid discharge. In this respect, the western coast is a good example where oolites clearly correlate with coastal oil and gas fields (Fig. 1). On the shelf near the Turali Point, there is a local accumulation of oolites; southward, they are encountered in the Dagogni–Kayakent (Bashly Point) sector; and further, only within the limits of the Bakinskii Archipelago (Klenova *et al.*, 1956, 1962). These authors also noted oil manifestations related to exposures of Chokrakian rocks in the Kayakent area.

There is also other evidence for the supply of abyssal fluids to the surface: during sampling of groundwater in lagoons on the Turali Point, gas spontaneously emanated from sand layers. The gas had nitrogen composition. In this case, a ratio of He isotopes ($^3\text{He}/^4\text{He} = 2.0 \times 10^{-8}$) measured in this gas rejects the mantle origin of He. Such a "crustal" value of $^3\text{He}/^4\text{He}$ is characteristic of most mineral (often thermal) springs of the coastal zone of Dagestan (Lavrushin *et al.*, 1996). In one of these springs—at the site of an unserviceable gas well at the margin of Berikei Settlement (Bashly Point, Dagestan)—we found oolites with a diameter of 3–5 mm, light color and radiate-fibrous structure of concentric layers.

On the eastern coast, oolitic sand accumulations are also observed south and north of Krasnovodsk (Turkmen-Bashi) and on the shelf of the Ogurchinskii Island and Cheleken Peninsula. Here, they associate with neotectonic uplifts and mud volcanism (Kholodov *et al.*, 1989; Lebedev *et al.*, 1975).

Light-colored oolites (from light gray to pink) predominate in this shelf area (to a water depth of 25–30 m). Dark-colored varieties are encountered here only as an admixture (Klenova *et al.*, 1956, 1962). At greater depths, like in the Northern Caspian Basin, dark-colored oolites form compact accumulations. They are also frequently found in mud breccias (Klenova *et al.*, 1956, 1962); an oolitic sand layer is formed on the tops of submarine mud volcanoes during a period of their quiescence.

The Neocaspian shore sediments are represented by light gray (almost white) fine-grained sand on the Cheleken Peninsula and south of it, on the shore of Turkmen Gulf over almost 300 km. The white color of the sand is caused by the presence of thin carbonate crust, covering silicate grains (Fig. 2g). This sand composes beach-ridges, coastal barkhans, and desiccated bays corresponding to the maximum level of the Neocaspian transgression in 1930. Wide distribution of carbonate ooid possibly indicates a mechanism of its formation differing from, for example, that in the Northern Caspian Basin. In the southern part of the eastern coast (in the Okarem Settlement area), sediments show an admixture of dark-colored oolites with well-expressed concentric layers (Fig. 2h). This fits well with the presence of a number of mud volcanoes close by the coast (Gek-Patlauk, Ak-Patlauk, and Keimir-Chikishlyar mud volcanoes).

Thus, oolitic sand fields often associate with fault zones and neotectonic structures where mud volcanism and groundwater discharge into surface sediment layers are located.

However, oolitic sand in the coastal zone and shelf of the southeastern shore, situated within a zone perspective for oil and gas and also characterized by mud volcanism, is most likely an exclusion, and their origin owes to other sources which is not related to discharge of internal fluids.

Oolitic Sand and Sites of Groundwater Discharge

The discussion about sites of subaqueous discharge is connected, first of all, with locations of mineralized deeply circulating water discharge. In the Caspian Sea, they are characterized by extremely variable gas and chemical composition. The methane-bearing water is most widespread. Its formation is related to the process of oil and gas generation. The most typical example is represented by mud volcanoes in Azerbaijan and Turkmenistan, as well as mineral waters from the coastal zone of Dagestan. Additionally to methane-bearing waters, there are CO₂-bearing mineral waters. Mineral-

ization of water varies within a wide range from weakly mineralized (~5–10 g/l) to salt brines (~200–250 g/l). The water is predominantly of the Cl–Na type, sometimes of Cl–Na–Ca or HCO_3 –Cl–Na types (Table 2, samples 40 and 41).

As mentioned above, oolitic sand was found in mud breccia of submarine mud volcanoes. We also observed several sites of fluid discharge with oolitic sand and carbonate cementation of sediments on the Dagestan (Bashly Point) and Turkmen coasts (Northern Cheleken Gulf, Southern Cheleken Sand Bank, and Uzunada Gulf in the central part of the Turkmen Gulf). Despite different thicknesses of the sand deposits, their sequences have many common features; the oolitic sand always marks the upper layer of coarse-grained sand corresponding to the last stages of regressive phases. Their thickness varies between tens of centimeters (the Turkmen coast) to 2–2.5 m (the Bashly Point). In all of these sequences (except for the Uzunada Gulf), the sampling of groundwater revealed discharge of deeply circulating fluids.

Chloride-sodium brines with a high content of Ca (up to 1.18 g/l) were noted in the northern Cheleken Gulf in sediments at a depth of more than 50 cm bsf (Table 2, sample 37b). It is evident that they do not have a marine origin but were delivered from the upper part of the red-colored unit, in which Cl–Ca–Na water with a concentration of Ca^{2+} of up to 16 g/l are developed. Above them (interval of 0–30 cm bsf), waters of marine (Cl– SO_4 –Na–Mg) type are observed, which are akin to samples 34–39 (Table 2). Their formation is a result of evaporation of marine water in a beach–lagoon zone (Dvorov, 1975, 1981, 1985). Sulfates are intensely reduced in this layer. The sand is colored in black, and a strong smell of H_2S is felt. Carbonate cementation forms at the boundary of the mixing of this water with the Cl–Na–Ca brines from the underlying sediment layer. The thickness of carbonate crust reaches 2–3 cm. Chemogenic carbonates are formed due to reaction of diagenetic CO_2 with Ca from deep-seated brines.

In deposits of the Southern Cheleken Bank, carbonate cementation of sediments and water of a nonmarine origin are also noted. The latter differs from marine water by high concentrations of HCO_3^- -ion but the absence of H_2S (Table 2, sample 50b). Therefore, the nonmarine water is similar to the fluid from mud volcanoes of Cheleken Peninsula and to water from other areas of mud volcanism manifestation (Dvorov, 1985; Rakhmanov, 1987).

The most dramatic example of the association of oolitic sand with sites of groundwater discharge is observed in a sedimentary sequence in the Bashly Point area (in a channel issued from the Adzhi Lake). The channel crosscuts a marine terrace and a beach ridge. The surface layer of sediments in this sequence is partially affected by eolian processes. The terrace rises 5–6 m above the sealevel. This suggests, according to

morphological evidence, its Neocaspian age (Rychagov, 1974; Varushchenko *et al.*, 1987).

In the channel, approximately 200–300 m of the coastline, there are seepages of thermal waters ($T = 40$ – 55°C ; Table 2, samples 40 and 41). In the channel wall, up to 4 m high, one can observe vertical sandy diapirs, several layers with carbonate cementation, and travertine (from 1–3 to 10–20-cm thick). This is overlain by an oolitic sand layer, 2–2.5-m thick, which is cemented by carbonate near the diapirs. The appearance of oolites in the upper part of the sequence coincides with the beginning of a regressive stage and a shift of intertidal zone toward the site of the thermal water discharge. Such a combination of oolitic sand and carbonate cementation in the sequence additionally proves the genetic relationship between these types of sediments.

Carbonate cementation was also noted in the Baku Archipelago, e.g., in the coastal zone of the Lebyazhii and Urunos islands (Klenova *et al.*, 1956, 1962). Here, the base of a carbonate cementation layer is marked by accumulation of oxides of iron and manganese. Because the hydrochemical sampling was not carried out, the authors interpreted the above observation as a result of chemogenic-diagenetic processes, not relating them to a discharge of groundwater (mud volcanic fluid).

Conditions of Formation of Carbonate Cementation and Oolites in Sediments of the Southeastern Coast

As noted above, oolitic sand is widespread on the Turkmen Gulf, marking the recent coastline and desiccation line of 1930 over a distance of approximately 300 km. It is unlikely that the oolitic sand was formed by a discharge of deeply circulating waters.

Oolitic sand of this region was redeposited several times under the influence of eolian and intertidal processes. Therefore, it is quite difficult to define its genetic affiliation with a certain type of coastal geomorphologic elements.

This problem can be elucidated by studying carbonate cementation crusts sometimes encountered among the sand. They form at places of the washout of beach–lagoon deposits. Their thickness rarely exceeds a few millimeters, and the area is only a few square centimeters. The sandy material is normally cemented during a washout of sand containing diagenetic H_2S -bearing water. This water differs from marine water by high concentration of HCO_3^- (Table 2, Samples 1–6 and 17–24). Biogenic processes of sulfate reduction, taking place in sediment, give rise to a decrease of pH in water from 8.4–8.2 to 7.1–6.5. In the process, part of carbonate material of chemogenic or biogenic origin dissolves. This results in an increase of calcium and magnesium ions in the pore water.

When such water approaches the surface, partial pressure of CO_2 decreases, and H_2S is oxidized to S^0 .

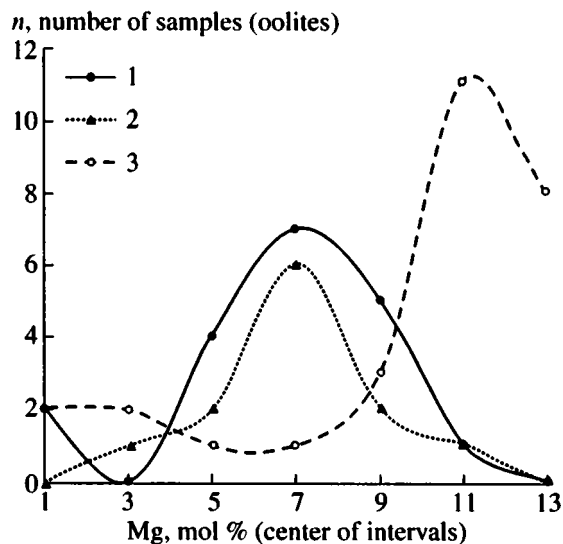


Fig. 4. Concentration of Mg in oolites from the Caspian Sea. Lines show the Mg distribution in oolites. (1) Dagestan coast; (2) Northern Caspian Basin; (3) southeastern coast of Turkmenistan.

This causes an increase of pH values, resulting in settling of chemogenic carbonate, which, in turn, cements sand grains.

The most favorable conditions for the realization of this scheme of carbonate cementation (and oolite formation) are produced in periods of unstable sealevel position. The near-shore sediment surface layer, affected by early diagenetic processes of biogenic sulfate reduction, is prone to reworking at the beginning of transgressive and especially regressive phases. The analogous conditions (only at much smaller scale) appear as a result of wing-induced surges.

Thus, all recorded cases of manifestation of carbonate cementation in the Caspian Sea sediments are, in one way or another, related to geochemical barrier in discharge zones of marine water, which was transformed during the early diagenesis, or deeply circulating water. More massive formations appear under influence of the deeply circulating water. The climatic factor in this case seems to play a minor part. These data indirectly argue for the connection of the formation of oolitic sand, which is genetically related to carbonate cementation, with sites of subaqueous groundwater discharge.

COMPOSITIONAL FEATURES OF CARBONATE MATERIAL IN OOLITES

Mineralogical Composition (General Remarks)

Investigations of chemical and mineralogical compositions of oolites from the Caspian Sea showed that they are not rigorously analogous to oceanic oolites (Sorokin *et al.*, 1987). As opposed to the oceanic oolites, which are made up of aragonite, Caspian oolites consist of Mg-calcite (5–8% MgCO_3). This is

probably explained by peculiarities of Caspian water composition that differs from an oceanic one by lower mineralization (almost 3 times lower) and larger (almost twice) values of coefficients of Mg/Cl and SO_4/Cl (Table 2, samples 17–24).

In ancient oceanic sediments, oolites usually consist of calcite with different composition or dolomite. The absence of aragonite in them is traditionally explained by postsedimentary transformation of carbonate material (Pettijohn, 1975; *Carbonates...*, 1983). However, the possibility of other geochemical conditions of carbonate sedimentation in ancient seas is rarely taken into consideration. The temperature regime and CO_2 concentration in the atmosphere are probably the most important and variable factors defining geochemical peculiarities of chemogenic carbonates, in particular, their mineralogical and chemical composition. The CO_2 content in the atmosphere was highly changeable (approximately by a factor of two) in past epochs and was significantly higher than today's content (Budyko *et al.*, 1985). At a high concentration of CO_2 in the atmosphere, partial pressure of CO_2 in water was also correspondingly higher, favoring the formation of chemogenic carbonates with exclusively calcitic composition.

Chemical Composition of Carbonate Material

Chemical composition of oolites from different regions of the recent Caspian Sea is not uniform. First of all, they differ by the **magnesium** content (Table 1). According to this indicator, they can be divided into two main groups (Fig. 4) and a third small group. The first, high-Mg¹ group (MgCO_3 10–12%) includes oolites of the southeastern coast. Such high Mg concentrations were recorded for the first time in sediments of the Caspian Sea. This is also confirmed by the X-ray diffraction data (the first basal reflection for such calcite is 3.002–3.004 Å). The second group (MgCO_3 6–8%) includes oolites from different areas of the basin and does not have a precise geographical location. In the histogram, one can distinguish also the third small group, which is characterized by an even lower MgCO_3 content of not more than 4% and approximately corresponds to an average composition of marine limestone. The third group also includes ancient oolites (Table 1, sample K3) and central nuclei of some oolites represented by altered fragments of fauna or clastic carbonates. The high stability of the composition of high-Mg calcite from the southeastern coast is worth noting. The dispersion of MgCO_3 is 1.2% for this sample and substantially higher (2.6) for the low-Mg carbonate.

It is evident that the compositional stability of group 1 oolites, sampled in a ~300-km-long segment of the

¹ By their mineralogical composition, all oolites of the Caspian Sea belong to the class of high-Mg calcites ($\text{MgCO}_3 > 4\%$), however, because they do differ by the degree of Mg content, further in the text these groups are denoted as "high-Mg" and "low-Mg" oolites.

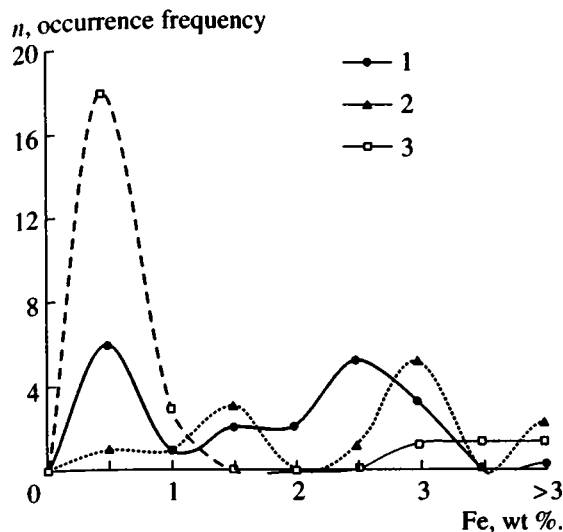


Fig. 5. Concentration of Fe in oolites from the Caspian Sea. Fig. 4 for the legend.

coast, testify to their formation from a chemically homogeneous medium under uniform conditions. The formation of oolites with such composition in a sedimentary sequence (in the zone of diagenesis) is unlikely, because pore water in the coastal zone of this area is highly variable in mineralization (from 25 to 200 g/l) and accordingly in Ca/Mg ratio, as well as in contents of H_2S and CO_2 at almost constant values of $pH = 6.8-7.2$ (Dvorov, 1981). The formation of these oolites is most likely to occur with the participation of marine water at the water-sediment boundary.

The high magnesium content in oolites from the southeastern coast is a reflection of the general hydrochemical zonality of the Caspian Sea. According to the data of Bruevich (1946), the highest salinity of water (up to 15 g/l) is observed in the Turkmen Gulf; from our data, it reaches 19 g/l in lagoons and shallow-water gulfs.

The concentration of iron in oolites varies within a wide range (FeO is from 0 to 7.5 wt %). The histogram shows a group with low concentrations of FeO (0–0.5 wt %). Its largest part is composed of oolites from the southeastern coast (high-Mg). The almost complete absence of Fe in them (<0.5 wt % FeO in 21 of 27 samples) seems to be related to the presence of a thick zone of hydrogen sulfide contamination in sediments; as a result, all iron capable of reactions is fixed in the form of sulfides. Ferruginous oolites are encountered only along the periphery of the area under consideration: in the north of Cheleken Island (Table 1, samples T32 and T71) and southward, in the area of Okarem Settlement (samples T103 and T123), i.e., where there are abrasion topography and manifestations of mud volcanism.

In oolites from other areas, the Fe admixture is rather unstable and can strongly vary even in a single

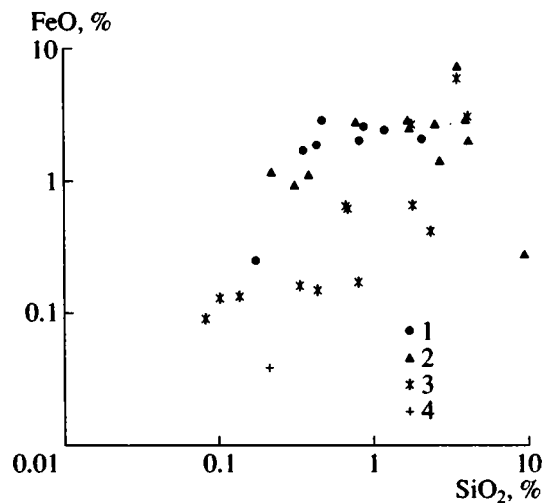


Fig. 6. FeO vs. SiO_2 in oolites from the Caspian Sea. Sampling sites: (1) western coast of the Middle Caspian Basin (Dagestan); (2) Northern Caspian water area; (3) southeastern coast of the Southern Caspian Basin (Turkmenistan); (4) Kara-Bogaz-Gol Spit.

sample (Table 1, samples C33, C223, and C236). However, there is an impression that, for oolites containing 6–8% $MgCO_3$, the Fe admixture is more typical than lower- and higher-Mg varieties (Fig. 5).

It is hard to judge from microprobe data whether this Fe is included in the crystalline structure of carbonate material or if it is present in the form of an admixture. The X-ray analysis also gives minor data on phase composition of Fe-bearing minerals because of their low concentrations and an admixture of terrigenous particles. However, some indirect data, such as the absence of evident relation to Mg concentration and the substantial variations of FeO in oolites from a single sample, most likely indicate that Fe does not belong to mineral structure of calcite composing concentric layers.

The indirect confirmation of this supposition comes from the evident correlation between FeO and SiO_2 in high-Mg oolites from the southeastern coast (Fig. 6). Silica compounds are likely to be represented mainly by fine clay material (possibly by newly formed) inside them. Such a correlation was not noted in other areas. In oolites from the Northern Caspian Basin and Dagestan, iron compounds are predominantly in oxidized form. Their yellow or brown color is particular evidence for that.

However, sometimes Fe is present in the isomorphic admixture. For example, Fe is partially present in reduced form and is probably involved in crystalline lattice of calcite of oolites from the central part of the Northern Caspian Basin (sample 33, no. 13 in Fig. 3). The composition of calcite is as follows: dry residue 10.34, R_2O_3 1.66, FeO 0.93, CaO 41.89, MgO 3.32, CO_2 37.06, total 92.0. Based on atomic absorption spectrophotometry, the MnO content is 0.21%.

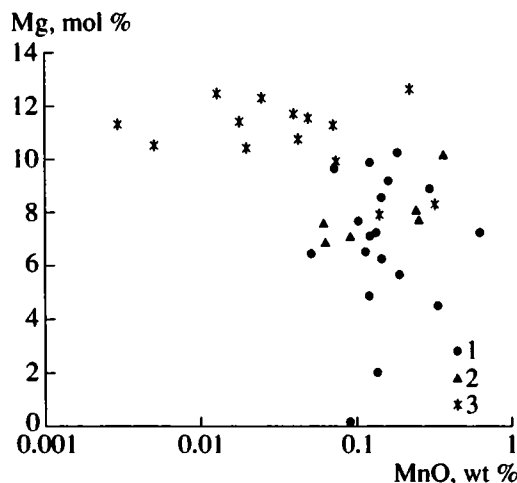


Fig. 7. Mg vs. MnO in oolites from the Caspian Sea. Fig. 4 for the legend.

The presence of Fe^{2+} in oolites is probably related to their postsedimentary transformation or specific sedimentation conditions.

Thus, the recent oolites from the Caspian Sea can be divided into two chemical types: low-Mg-ferruginous (FeO 2–3 wt %; MgCO_3 6–8%) and high-Mg, Fe-free (FeO < 0.5 wt %; MgCO_3 10–12%) (Table 1). As this takes place, Fe is most frequently present in carbonate concentric layers in the form of a terrigenous admixture. A local increase of Fe (and Mn) concentration frequently is one of the indicators of subaqueous discharge. Hence, the presence of Fe in carbonate concentric layers may indicate the genetic relation of "ferruginated" or "dark-colored" oolites to the sites of deep-seated fluid discharge.

The genetic relation of carbonate cementation to oolites is confirmed by chemical study (Sorokin *et al.*, 1987). Calcite from a carbonate crust (from the Baku Archipelago area) contains 5–8% MgCO_3 ; thus, it does not differ in chemical composition from oolites of the western Caspian coast. We obtained similar results for thin carbonate crusts from the southeastern coast (Table 1, samples 33/90 and 33/90d).

Based on EPMA data, a number of elements, such as Si, Al, Na, Mn, P, and S, are constantly present in the composition of oolites.

A concentration of Mn is usually low (MnO not more than 0.62 wt %; Table 1). Its content in carbonate material, at first glance, is inversely correlated to Mg concentration (Fig. 7). This seems to be the result of the general tendency toward transformation of Mg-calcite during a diagenesis, i.e., partial dissolution of magnesium component and its replacement by carbonate with a complex composition, containing Fe and Mn additionally to Mg (Carbonates..., 1983). However, if the whole sample subdivides into two groups (the first one includes samples from the southeastern coast; the sec-

ond one contains all the rest), one can be convinced that, within each group, the correlation between MgO and MnO disappears. The distinguished groups do not overlap each other in the plot. Hence, the noted above dependence emphasizes geochemical differences in the initial conditions of the formation of oolites in separate places of the basin rather than in the trend of postsedimentary transformations of carbonates.

Three specimens from the southeastern coast are distinguished by a high Mn content (0.14–0.32 wt % MnO). Two of them are characterized by a lowered Mg content (MgCO_3 ~8%) and accordingly do not belong to this sample (they were collected on the periphery of the area and mentioned earlier). The third specimen was taken from the base of an oolitic sand layer (at a depth of 2.5 m), where the findings of oolites are rare. The studied oolites might have been partially altered or they could have formed under other geochemical conditions.

It is hard to judge the forms of manganese occurrence. In most cases, it probably exists in the form of oxides in the composition of terrigenous admixture (this is indirectly confirmed by the absence of the inverse correlation between Mn and Mg; Fig. 7). At the same time, the X-ray analysis of sample 33 (Northern Caspian Basin) showed that Mn, like Fe, can be involved with a crystalline lattice of calcite. The systematic suppression of calcite reflections is seen in the X-ray diagram (Fig. 8). Values of the obtained interlayer distances correspond to Mn-calcite with a complex composition (%): MnCO_3 7, MgCO_3 2.57, and FeCO_3 3.5 (diagnostic reflections at 3.020, 1.903, and 1.862 Å) (Mikheev, 1957).

The X-ray data contradict the data of chemical composition based on microprobe analysis (Table 1, sample 33) and chemical analysis. A MnO content in the sample is not more than 0.35 wt %, that is approximately 5 times less than the expected value (1.5 wt % MnO). A Fe^{2+} concentration is also lower almost by a factor of two: FeO = 0.93 wt % (1.9 wt %, based on stoichiometry). This discrepancy seems to be explained by the presence of two phases of carbonate material: well-crystallized Mn-bearing variety and poorly crystallized Mg-bearing variety. Evidently, Mn is irregularly distributed through the entire volume of concentric layers and enters only in composition of local Mn-calcite segregations. The high degree of crystallinity of Mn-calcite indicates its postsedimentary origin.

This conclusion agrees well with data of Shul'ts (1962), who pointed out an irregular coloring of carbonate concentric layers. However, he related dark areas in oolites to the painting of concentric layers with organic matter, because Fe was not detected in his study. Our data on the chemical composition of oolites indicate, by contrast, that their dark color is conditioned by the presence of chromophoric elements (Fe and Mn). Their compounds paint oolites at surface (films of oxides) and inside the crystalline lattice of Mg-calcite.

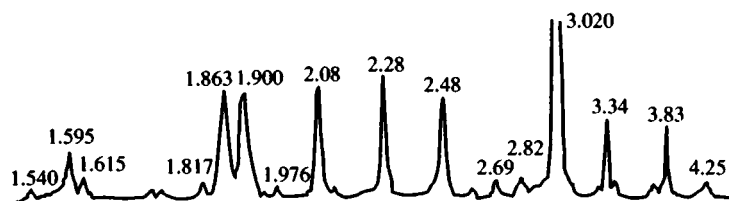


Fig. 8. X-ray powder diffraction pattern of oolites from the Northern Caspian Basin (sample 33, northwest of Kulaly Island).

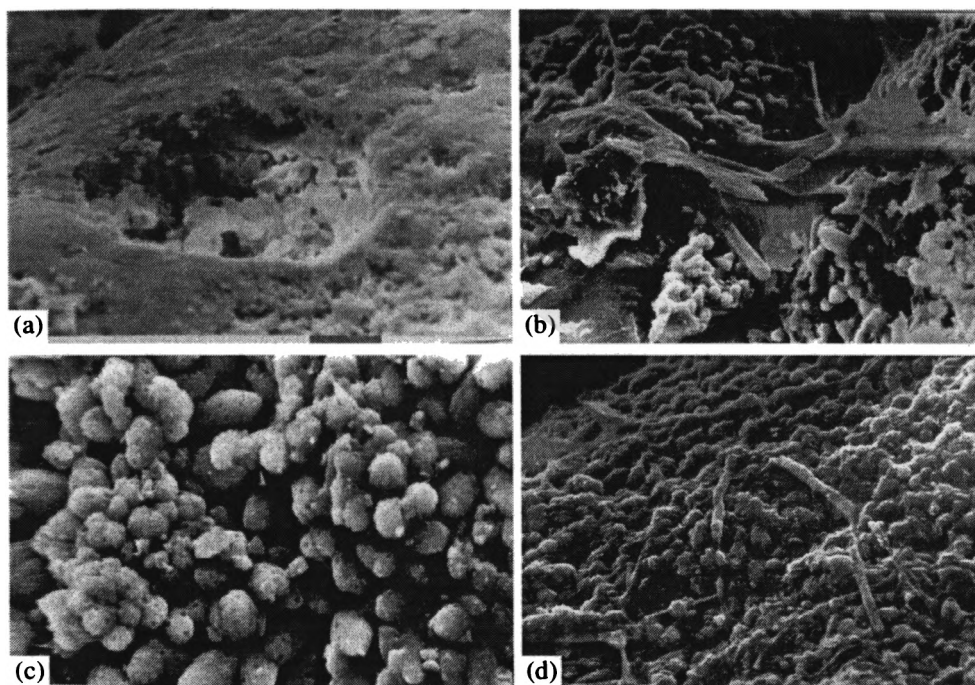


Fig. 9. Photomicrographs of the (a) surface of oolite grains and (b-d) crust of carbonate cementation; the southeastern coast of the Caspian Sea (area 2 in Fig. 1).

A small admixture of **silicon and aluminum** is characteristic of all types of oolites. This is stipulated by their formation in active hydrodynamic conditions (capturing of silicate particles by outgrowing concentric layers) (Table 1). As noted above, in oolites from the southeastern coast, Si and Fe concentrations correlate between each other, possibly indicating the formation of secondary silicate mineralization in carbonate concentric layers. Conditions of their formation could be realized during an early diagenesis, where Fe can pass into the mobile Fe^{2+} form under reducing conditions. However, pore water of the Turkmen coastal zone is characterized by extremely high concentrations of Si (SiO_2 up to 70 mg/l). The Si concentration directly correlates with the degree of biological activity of sulfate-reducing bacteria and, accordingly, on concentrations of H_2S and HCO_3 in water (Table 2).

High-Mg calcite form characteristic foliated, isometric microcrystals (Fig. 9a). The imperfection of their crystalline form can be explained by structural defects related to inclusions of hydrated ions of Mg in

crystalline lattice of calcite. Part of these defects, as well as high solubility of Mg-calcite, many authors relate to the presence of ions of Na and sulfate in a crystalline lattice (Berner, 1976; *Carbonates...*, 1983). We found a direct correlation between concentrations of Na and Mg in oolites (Fig. 10). Unfortunately, it is impossible to judge the trend in changes of sulfate concentration on the basis of the data available; however, a detectable admixture of sulfate is often noted in carbonates from the southeastern coast (Table 1).

Determinations of P were random and were carried out only for oolites from the Northern Caspian Basin and the spit of the Kara-Bogaz-Gol Gulf. The P_2O_5 content in them varies from 0.45 to 0.9 wt %.

ISOTOPIC COMPOSITION OF CARBON AND OXYGEN FROM OOLITES

The results of isotopic investigations (Table 3; Fig. 11) showed that oolite-bearing sediments in the Caspian Sea are characterized by wide variations of isotopic

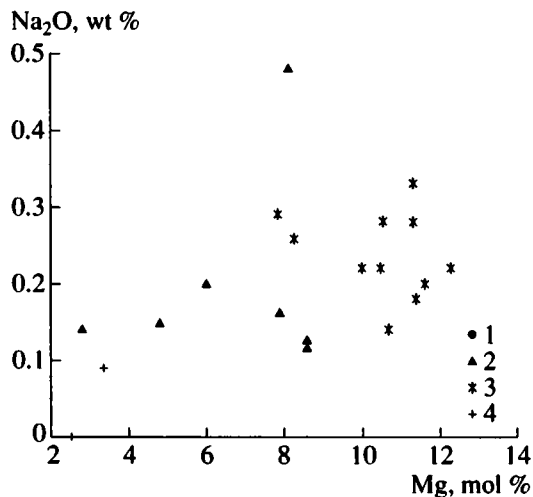


Fig. 10. Na_2O vs. Mg in oolites from the Caspian Sea. Fig. 4 for the legend.

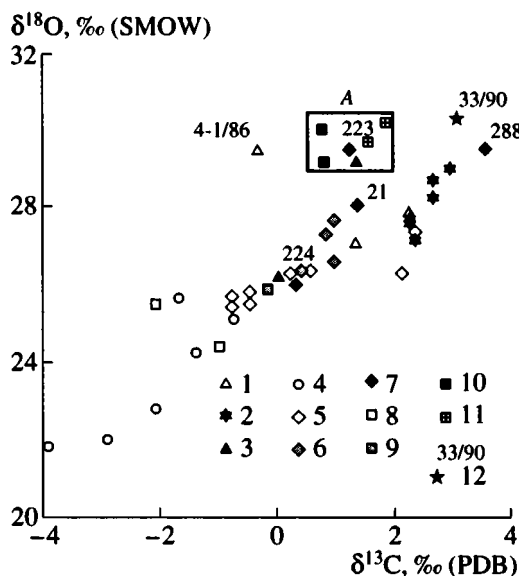


Fig. 11. Distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in oolites from the Caspian Sea. (1) Turkmenistan (Cheleken Peninsula); (2) Southern Caspian Basin, southeastern coast; (3) southeastern coast; (4) Northern Caspian Basin; main field of oolites; (5) northeastern zone, (6) central zone, (7) southwestern zone; fauna; (8) northeastern oolite zone, (9) central oolite zone, (10) southwestern oolite zone; (11) fauna from the southeastern coast of the Southern Caspian Basin; (12) carbonate cementation crust, northern Cheleken Gulf. (Area A) isotopically heavy carbonates.

menistan). Other sediments occupy an intermediate position in this plot.

The isotopic composition of oolites from the Northern Caspian Basin is not constant either. For instance, the lightest isotopic composition is found for carbonates from the northeastern zone: $\delta^{13}\text{C} = -0.8$ to $+2.1\text{‰}$ and $\delta^{18}\text{O} = 22.5$ – 26.3‰ ; the heaviest one is observed in the southwestern zone: $\delta^{13}\text{C} = 0.3$ – 3.5‰ and $\delta^{18}\text{O} = 26.0$ – 29.5‰ . Oolites from the central zone are isotopically in an intermediate position: $\delta^{13}\text{C} = 0.4$ – 0.9‰ and $\delta^{18}\text{O} = 26.3$ – 27.6‰ (Table 3; Figs. 3, 11).

In the plot (Fig. 11) constructed in coordinates of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$, the experimental values form a elongated field trending from the area of the highest values of $\delta^{13}\text{C} = 3$ – 4‰ and $\delta^{18}\text{O} = 29$ – 30‰ towards the lowest values with $\delta^{13}\text{C} = -3$ to -4‰ and $\delta^{18}\text{O} = 21$ – 22‰ . The main and probably the only reason of the observed linear dependence in isotope ratios are due to different conditions of their formation (salinity, temperature, and isotopic composition of water and dissolved bicarbonate).

At present, the isotopic composition of oxygen in the hydrosphere of the Caspian Sea is known in detail (Brezgunov *et al.*, 1987; Gorbarenko and Nikolaev, 1974; Ferronsky *et al.*, 1996). The principal regularities of the distribution of oxygen isotopic composition in the surface layer and water column of the Caspian Sea are revealed. It was shown (Brezgunov *et al.*, 1987) that an average isotopic composition of Caspian water characterizes a stationary isotopic state of an enclosed basin under certain climatic conditions, in which an evaporation is almost equal to fresh water input. Oxygen isotopic composition of water is closely related to salinity and is defined by a mixing of marine and fresh waters. The lowest values of $\delta^{18}\text{O}$ are noted in the Northern Caspian Basin (up to -8 or -9‰) and near the coast line. The central areas of the Middle and Southern Caspian basins are characterized by the heaviest oxygen isotopic composition.

Dorofeeva *et al.* (1996a, 1996b) executed a study of carbonate material in molluscan shells in order to elucidate the principal criteria for determination of paleosalinity of marine basins. They proposed an original method of a double carbonate thermometer, based on the parallel study of isotopic composition of oxygen and Ca/Mg ratio in an analyzed sedimentary specimen of carbonate material. The results of the investigations suggested that the isotopic composition of oxygen in the Caspian Sea is closely related to salinity and is dictated by processes of evaporations and fresh water input.

As known, oxygen isotopic composition in molluscan shells is defined by temperature and isotopic composition of water. In enclosed basins, the representative of the Middle Caspian Basin, biogenic carbonate formation has a number of specific features. According to Gorbarenko *et al.* (1975), these features imply that in basins of such type, oxygen isotopic composition in

composition of carbon and oxygen: $\delta^{13}\text{C}$ changes from -3.9 to 3.5‰ , and $\delta^{18}\text{O}$ changes from 21.8 to 29.5‰ . In the Caspian water area, isotope ratios are controlled by a spatial position of sampling sites (Fig. 11). The lowest values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are typical of oolites of the Northern Caspian Basin, and the highest values are recorded in oolites from the southeastern coast (Turk-

molluskan shells is defined mainly by isotopic composition of oxygen in water rather than by temperature of carbonate formation. Hence, oxygen isotope ratios in fossil mollusks from such water basins are not suitable for paleotemperature reconstructions, but they allow us to judge temporal fluctuations of isotopic composition of water from this paleobasin and its distribution over the area of the basin.

Thus, taking in mind the results of the previous isotope investigations, which allowed the main peculiarities of distribution of oxygen isotopes in hydrosphere and carbonate material of Caspian mollusks to be revealed, the established regularity of distribution of isotope ratios of carbon and oxygen in carbonate material of oolites becomes understandable. It is evident that oxygen isotopic composition in oolites must be entirely defined by oxygen from water in the hydrosphere (having regard to temperature of carbonate formation). For instance, the lightest oxygen isotopic composition is detected in oolites near the northern coast of the Northern Caspian Basin, where the highest enrichment of marine water in light oxygen isotope is recorded as a result of fresh water supply.

Oolites form the central part of the Northern Caspian Basin are characterized by intermediate values of isotopic composition of carbon and oxygen. This is defined by their geographic location at the boundary of the mixing of freshened Northern Caspian and more salty Middle Caspian waters. Oolites from the Southern Caspian Basin have a higher isotope ratios of carbon and oxygen. Here, the relative input of fresh water is at a minimum.

Among the studied groups of different oolites, in which the identification of many cases is arbitrary (e.g., the southwestern oolite zone in the Northern Caspian Basin and oolites from Cheleken Peninsula), appreciable variations of isotope ratios are sometimes observable. These variations seem to be caused by local isotope-geochemical conditions of sedimentation (such as isotopic composition of water, its temperature, and salinity).

Mollusks from the southeastern coast of the Southern Caspian Basin form a separate group (in terms of isotopic composition). This group also includes mollusks and oolites of the southwestern zone of the Northern Caspian Basin and separate oolites from the southeastern Caspian coast. Carbonate material in this group is characterized by heavy isotopic composition of carbon and oxygen, and forms a separate field A on the plot (Fig. 11).

It is worth noting that there is some statistic mean difference in isotopic composition of carbon and oxygen from mollusks and oolites within the same sampling areas. For instance, in the northeastern zone of the Northern Caspian Basin, isotopic compositions of carbon and oxygen in molluskan shells are lighter by ~1.2 and 0.2‰, respectively, than those in oolites. In the central zone, the corresponding differences are 1.0 and

1.0‰; in the southwestern zone, they are 0.8 and 1.0‰. Currently, it is hard to unambiguously explain this phenomenon which may be related to different temperatures of carbonate formation, different isotopic composition of near-bottom water (mollusk habitat) and sediments, different coefficient of fractionation in the bicarbonate and carbonate-ion system during formation of molluskan shells and oolites (which can have a biogenic nature, being the products of vital activity of cyanobacteria assemblages), etc.

Thus, the distribution of isotopic composition of carbon and oxygen in carbonate material of oolites and mollusks in the Caspian Sea corresponds to a linear function, and is probably defined by the interval of the mixing of bicarbonate marine ($\delta^{13}\text{C} = 3\text{--}4\text{‰}$; $\delta^{18}\text{O} = 29\text{--}31\text{‰}$) and fresh ($\delta^{13}\text{C} = -4$ to -3‰ ; $\delta^{18}\text{O} = 22\text{--}23\text{‰}$) waters. Additionally, there is a certain group of carbonate material both in oolites and in fauna (area A; Fig. 11) with heavy isotopic composition of carbon and oxygen. The presence of such carbonates may be stipulated by the interaction of complex processes taking place under conditions of the enclosed basin and arid climate. In the same geographic (and paleogeographic) conditions, some factors such as evaporation, supply of fresh water, and hydrodynamic regime, may result in the formation of local isotope-geochemical systems, leading to the appearance of carbonates with different isotopic composition.

When interpreting isotope data, the elucidation of the studied oolite age has great importance. Sometimes, we may deal with older carbonates from reworked sediments on the seafloor. In such a case, isotopic composition of oolites is characterized by paleoenvironment of their formation time, and may significantly differ from the recent isotope-geochemical conditions of sedimentation. To resolve this problem, special investigations are needed.

Thus, the results of isotope studies show that the formation of oolites in the Caspian Sea is most likely to occur directly from bicarbonate of near-bottom water (or from water in the upper layer of sediments) and, accordingly, is defined by the isotopic composition of seawater. However, the statistically significant dependence of values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ on chemical composition of oolites, particularly their Mg content, was not established. Presently, we can only assume some trend toward the increase of $\delta^{13}\text{C}$ with the increase of Mg content in carbonate material.

Diagenetic processes and oxidation of organic matter during sulfate reduction in sediments are also scarcely affect values of $\delta^{13}\text{C}$ of carbonate material in oolites. Incidentally, within the sedimentary sequence (to a depth of 3 m), these processes, characteristic of marine deposits of the southeastern coast, practically do not appreciably influence the isotopic composition of carbon and oxygen in carbonates (Kuleshov and Lavrushin, 1999). The correlation of the isotopic composition of carbon in oolites with the distribution of

hydrocarbon fields is not found either. At the same time, one can note a systematic difference of the carbon isotopic composition in oolites from that in recent fauna, sampled from the same sand.

This brings up another point: are deep circulating waters capable of influencing isotopic composition of carbonates at places of their subaqueous discharge? Some insight concerning this problem is provided by the results of carbonate sediment investigations from the coast of Dagestan and the northern Cheleken Gulf.

In travertine from Dagestan (a channel in the Adzhi Lake, Bashly Point), we found isotopic signs of oxidized carbon participation from hydrocarbons in the process of carbonate formation. The travertine is characterized by an anomalously high value of $\delta^{13}\text{C} = 10.5\text{‰}$ with a "normal marine" composition of oxygen ($\delta^{18}\text{O} = 28.9\text{‰}$). Here, carbon dioxide is probably formed as a result of microbial decomposition of methane, which led to the formation of isotopically heavy carbonates (Pokrovskii, 1980). At the same time, oolites and carbonate cementation formed in the surface layer of sediments, evidently at the contact with seawater, are similar to their isotope characteristics to oolites from the Northern Caspian Basin.

The analogous situation is observed in the northern Cheleken Gulf, where carbonates, originated at the boundary of the mixing of ground and marine waters, correspond by their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values to carbonates from salty lagoons, additionally confirming an idea that the main source of carbon dioxide is related to marine deposits. An excess of CO_2 results from biogenic sulfate reduction and processes of dissolution of carbonates contained in sediment. Carbonates are formed during a mixing of these waters with the underlying chlorine-calcium brines.

According to our point of view, these examples show a high buffer role of marine water, which removes all isotope records in carbonates, settling in a zone of mixing of marine and groundwaters. Therefore, one can suppose that isotopic methods cannot always be effective for elucidation of chemogenic carbonate genesis, forming in marine basins.

THE ROLE OF CYANOBACTERIAL ASSEMBLAGES IN FORMATION OF OOLITES

Evidence for bacterial activity is constantly observed when investigating oolitic sand. For example, remains of filamentous algae are recorded in oolites of the Northern Caspian Basin (Shterenberg *et al.*, 1975). We also found algae films on the surface of high-Mg oolites and in the crust of carbonate cementation from the southeastern coast (Fig. 9).

However, a question does arise of whether or not the vital activity of blue-green algae is the controlling factor for oolite formation, or their remains are merely captured during the outward growth of concentric layers, like terrigenous particles? The last supposition has

a certain basis, because oolites are formed on the surface (or near surface) of sediment, where microbial activity is extremely high.

Experiments showed that life organisms and products of their mineralization can not provide the formation of dense carbonate shell of oolites (Krylov *et al.*, 1986). As a result, only the formation of a delicate, fragile carbonate cover is possible on the surface of particles. This cover would be quickly destroyed in a hydrodynamically active environment. The formation of dense carbonate concentric layers occurs only against the background of active processes of chemogenic carbonate sedimentation.

The study of thin sections of sediments from the Northern Caspian Basin revealed that "filamentous algae" canals, found in concentric layers of oolites, may be a result of the vital activity of borer-algae, because the same features are noted in some faunal fragments as well. These observations are contradictory to the concept of a decisive role "filamentous algae" in the oolite formation (Shterenberg *et al.*, 1975). Furthermore, the isotope study of carbon and oxygen has not shown the involvement of blue-green algae in the formation of carbonate layers of oolites.

Thus, colonies of blue-green algae probably provide some degree of order in structure of chemogenic carbonates, enhancing a fixing of calcite (or aragonite) on the surface of sand grains, which, finally, results in oolite formation.

CONCLUSION

The obtained data do not exclude the possibility of participation of mineral waters in the formation process of local accumulations of oolites (first, their low-Mg varieties).

This process can even play a relief-forming role. During the accretion of carbonate layers to terrigenous particles, the size of the latter increases on the average by a factor of 1.5–2. As a result, a sandy layer will swell in proportion to the increase of particle diameter. This can lead to the formation of local elevations, sand banks (or increasing of their elevation if they were already developed). The thickness of oolitic sand sequence in the Caspian Sea Basin often reaches several meters, which is enough to provide the formation of the above mentioned sand banks in the Northern Caspian Basin, having a relief of about 5 m. In this case, these banks may reasonably have a "geochemical" nature rather than tectonic origin which was previously assigned to them (Leont'ev, 1957; Malovitskii, 1970). Their growth could be caused by local chemogenic mineral formation. Carbonate cementation, accompanying oolites, would evidently prevent these positive structures from being eroded. The increase of grain size will favor this as well.

However, it should be recognized that this current hypothesis is largely based on indirect observations and

is not confirmed by direct facts. The lithological study of the upper layers of sediments, recovered by gravity corers from the above mentioned topographic features and analyses of chemical composition of pore waters, are needed for the confirmation.

According to all of the above, the following conclusions can be drawn:

(1) Neocaspian sediments incorporate two types of carbonate oolites, differing in chemical composition: low-Mg and high-Mg. By and large, their isotope-geochemical features correspond to general climatic and hydrochemical conditions in the Caspian Sea Basin. However, this does not explain the reason for local existence of oolites in some areas of the sea.

(2) There is a spatial correlation of the fields of low-Mg oolitic sand with tectonically weak zones and recent anticlinal uplifts located in oil- and gas-bearing areas.

(3) High-Mg oolites from the southeastern coast are most likely to form at regressive stages of the sea basin evolution (without participation of deeply circulating waters).

(4) Minor elements (Mn, Fe, and Si) in composition of oolites have principally sedimentogenic origin and are captured by carbonate concentric layers in the process of their outward growth. During the early diagenesis, Fe and Mn can enter the crystalline lattice of calcite.

(5) Variations of isotopic composition of carbon and oxygen in oolites are dictated by isotope-geochemical characteristics of marine water and bicarbonate dissolved in it. At the same time, oolites from the Caspian Sea notably differ by their isotopic composition from the recent carbonate fauna.

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Polycyclic Aromatic Hydrocarbons in Volcanic Rocks and Hydrothermal Minerals from Iceland

A. P. Geptner*, T. A. Alekseeva**, and Yu. I. Pikovskii**

* Institute of Geology (GIN), Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 109017 Russia

** Geographical Faculty, Moscow State University (MGU), Vorob'evy gory, Moscow, 119899 Russia

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Abstract—The composition and specific features in the distribution of polycyclic aromatic hydrocarbons (PAH) in volcanic rocks and hydrothermal minerals have been considered. It has been shown that the total PAH amount determined in hydrothermal mineral complexes is 1–2 orders of magnitude higher than in unaltered rocks. In this case, various mineral associations differ in the content and in the composition of PAH. The conducted investigation suggests that the composition and distribution of hydrocarbons in volcanic and hydrothermal formations are governed by physicochemical conditions of the consolidation of volcanites and secondary mineralogenesis, rather than by any local features of the geological structures. Hydrocarbons in the volcanic and postvolcanic processes have been supposedly connected with the endogenic supply of carbon and hydrogen.

Findings of carbon compounds, such as hydrocarbons and bituminous formations, in volcanic rocks have attracted the attention of investigators for a long time. This is connected with the discussion concerning the role of volcanism in the formation of the Earth's crust and atmosphere, the generation mineral deposits, and the appearance of the organic world on the Earth (Markhinin, 1985; Ronov, 1976). The presence of methane and other gaseous hydrocarbons in fumaroles and hot springs of present-day volcanic fields in various regions of the world are widely known facts (Taran, 1984; White and Waring, 1963). The condensation of liquid petroleum from superheated vapor on the surface of groundwater was reported from thermal fields of the Uzon Volcano caldera on Kamchatka (Karpov and Pavlov, 1976; Naboko, 1974; Pikovskii *et al.*, 1987). Similar petroleum shows were noted in fumarole springs of the Yellowstone Park and adjoining Northwestern Wyoming territory (USA) (Clifton *et al.*, 1990). There are references to the findings of liquid petroleum drops and solid bitumens directly in solidified lavas and volcanic bombs of young and ancient eruptions (Kudryavtsev, 1959). Volcanic rocks are presently regarded as a source of commercial resources of hydrocarbon gas (Kuuskraa *et al.*, 1998).

Investigations of dispersed organic matter in volcanic ash, eruptive flow fillers, volcanic bombs of volcanoes located on Kamchatka, Kuril Islands, and in Indonesia have shown that the volcanogenic carbon-bearing substance represents a multicomponent mixture of compounds with a relatively complicated composition, consisting of acyclic and cyclic hydrocarbons, amino acids, amino sugars, carbohydrates, porphyrins, and other compounds (Markhinin, 1980, 1985; Podkletnov, 1985). The mentioned authors indicate that 60 individual molecules and 14 groups of compounds with non-

decoded or incompletely decoded compositions are identified in the volcanic formations collected by them.

Works on the study of polycyclic aromatic hydrocarbons (PAH) contained in the products of volcanic activity started to appear since the second half of the 1970s. Such hydrocarbons are interesting as geochemical indicators of hydrocarbon flows in the lithosphere (Pikovskii, 1993) and as sources of environmental pollution by carcinogenic substances. Benzo[ghi]perylene, benzo[a]pyrene, naphtho[1,2-k]fluoranthene, and traces of coronene have been identified in ash from Alaid Volcano, whereas the acenaphthene-type structures, fluoranthene, and pyrene were additionally detected in ash from Tolbachik Volcano (Florovskaya *et al.*, 1978). The content of benzo[a]pyrene in volcanic ash from different volcanoes varies considerably. It was 0.3–0.4 ng g⁻¹ in ash from Tyatya Volcano (Kunashir Island) and from the southern crater of Ploskii Tolbachik Volcano (1976, Kamchatka), whereas in the Northern breakthrough of the same volcano (1975), the benzo[a]pyrene content was 5–6 ng g⁻¹ (Il'nitskii *et al.*, 1977). In small slag bombs collected in the ashfall from the Southern breakthrough of Ploskii Tolbachik Volcano (November 1975), the content of benzo[a]pyrene amounted from 2 to 4 ng g⁻¹, whereas slag bombs from the lava flow (at the same place, April 1976) amounted to 0.45 ng g⁻¹ (Il'nitskii, 1977).

Recent investigations have demonstrated that polycyclic aromatic hydrocarbons are abundant in modern and ancient volcanic rocks. The "volcanic association of PAH" has been identified with fluorene and biphenyl as typomorphic compounds (Gennadiev *et al.*, 1996). Various viewpoints have been expressed about the origin of hydrocarbons in general and PAH particularly in

volcanic rocks. In many cases, hydrocarbons and their derivatives are believed to be introduced into volcanic rock masses by later postvolcanic solutions. Carbonaceous compounds in such solutions appeared due to hydrothermal activity (Florovskaya *et al.*, 1986) or to their release from lateral rocks. When sedimentary rocks or recent sediments and soils are heated up by lava flows, the organic matter sublimation and neogenesis of PAH become possible. At the same time, there are indisputable evidence that the synthesis of hydrocarbons takes place directly during the volcanic process. The hypothesis about the origin of hydrocarbons due to volcanic emanations was primarily put forward by E. Coste as early as the beginning of our century (Coste, 1904). Mukhin *et al.* (1976) and Taran *et al.* (1981) have experimentally proved that the synthesis of hydrocarbons is possible in conditions simulating the volcanic activity with the use of volcanic rocks as a catalyst of the process. Chemical conditions of the formation of hydrocarbons in the ash-gas column of the volcanic eruption have been studied by Podkletnov (1985).

At the same time, hydrocarbons in rocks and secondary minerals of such a classical volcanic region as Iceland have not been specially studied. The data on a relatively small methane content in hydrothermal fumaroles and gases in Iceland have been known (Armannsson and Kristmannsdottir, 1992; Arnorsson, 1987; Arnorsson *et al.*, 1987; Kristmannsdottir, 1991). According to the data reported in the work of Kononov (1983), methane was most abundant in the hydrogen-type therms. Its maximum amounts were detected in two samples from the Hengil region and equalled 4.2 and 10.8 vol %. The methane content in hydrogen therms of Iceland is usually much less than 1 vol %. The content of heavy hydrocarbons was determined in 11 selective samples from hydrotherms of different types; C_2H_6 was found almost in all of the samples and amounted to 0.002 vol %, C_3H_4 was found in three samples and amounted to 0.0005 vol %, C_3H_8 was found in five samples and amounted to 0.0004 vol %, C_4H_4 was found in a single sample and amounted to 0.0002 vol %.

The first single finding of a large asphaltite segregation (6–7 cm³) was recently registered in the Miocene (about 5 Ma) plateau-basalt in Southeastern Iceland (Jakobsson and Fridleifsson, 1990). Asphaltite was located in large cavities of the 6-m-thick lava flow. A thin (60–80 cm) layer of lignite was detected below lavas. Asphaltite in amygdulites fills interstices between quartz crystals or is met at the bottom of amygdulites in the shape of spherical bodies (2–8 mm in diameter) that are usually covered by fine quartz crystals.

The study of the secondary mineralization of lavas enclosing the bituminous substance has made it possible to distinguish three hydrothermal episodes. The first one is connected with the burial metamorphism, when low-temperature minerals, such as siderite, opal, zeolite, smectite, calcite, celadonite, and iron oxides, were formed. The temperature of this association formation

has been estimated at 40–80°C. During the second hydrothermal episode, the rock sequence was washed by waters with a higher temperature (80–120°C), and calcite and siliceous minerals (agate, quartz, and jasper), pyrite, and possibly tridymite were formed in cavities. During this period, lignite and the overlying lava bed were at a depth of 300–500 m from the Earth's surface. The regional zeolitization (the third hydrothermal episode) is related to the subsequent subsidence and accumulation of a thick lava sequence (about 1 km). A sill 30–70 cm thick supposedly intruded into lignite during this period. A close contact of lignite with the sill and similar results of the isotope analysis of carbon from lignite and asphaltite ($\delta^{13}C = -27.67$ and -27.07% , respectively) allowed us to conclude that the bituminous substance was formed due to the heating of lignite by the sill intrusion.

Jakobsson and Fridleifsson (1990) identified seven polycyclic aromatic hydrocarbons (phenanthrene, pyrene, benzo[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, and benzo[ghi]perylene) in a sample of asphaltite by the gas chromatography method (the analysis was accomplished in the Geological Survey of the USA by K.A. Kvenvolden). Any data on their quantitative relationships have not been reported.

Earlier, PAH were identified near the coasts of Iceland in bottom deposits of the Atlantic Ocean (Florovskaya *et al.*, 1980). Benzo[a]pyrene and its derivatives, benzo[ghi]perylene, perylene, and coronene were detected in insignificant quantities in silts by the Spol'sky spectroscopy. Coronene was met only at a single observation station in the Denmark Strait.

This work is devoted to the results of identification and study of the PAH distribution in volcanic rocks and secondary minerals from different regions of Iceland in order to establish the character of distribution, conditions of formation, and possible sources of these hydrocarbons.

MATERIALS AND RESEARCH METHODS

Geological characteristics of the objects of investigation. Polycyclic aromatic hydrocarbons were studied in fresh and altered volcanic rocks, as well as in secondary minerals from the smectite-zeolite zone of hydrothermal alteration. The samples for investigation were selected from different regions of Iceland (Fig. 1).

Iceland is built by volcanic, predominantly continental rocks, consisting of basalts to the extent of above 90%. Sedimentary rocks (mainly the products of glacial and fluvioglacial activity) play an insignificant role. Thin interlayers of coal and lignite are rare. The Miocene-Pliocene volcanic rocks subsided below the groundwater level are presently altered to a variable extent by heated groundwater. Most intense alterations (e.g., the propylitization zone) have been observed in the bodies of large central volcanoes including acid

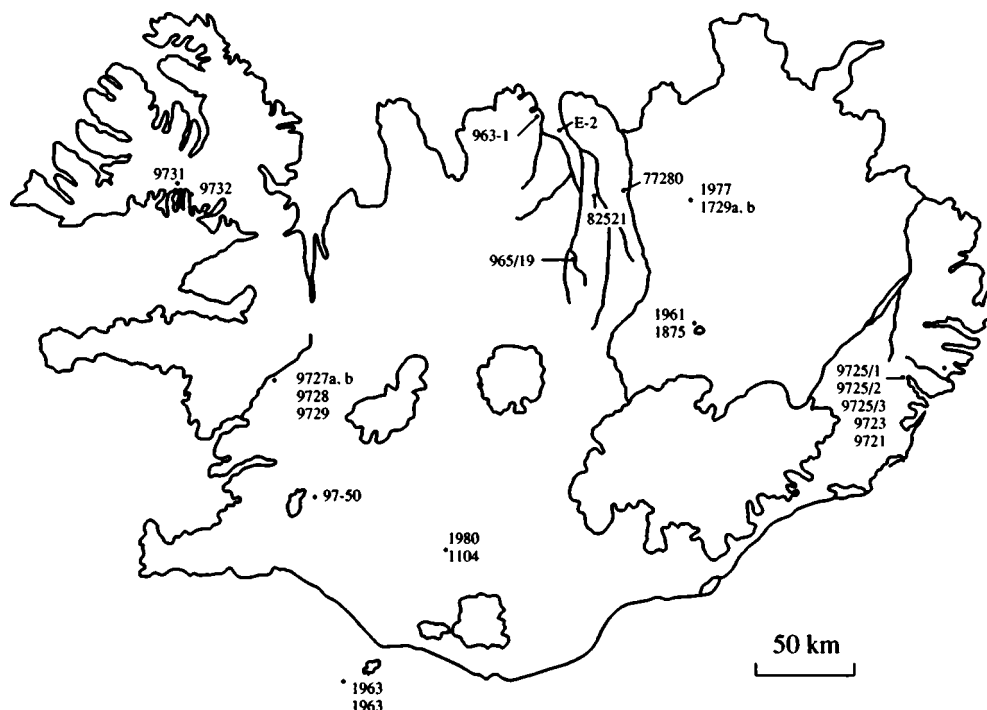


Fig. 1. Number and location of investigated samples.

subvolcanic intrusions. Plateau-basalts are altered non-uniformly beyond them. Groundwater intensely affected host rocks in the zones of fissure swarms, spatially conjugating with large volcanic edifices. Various mineral associations can be identified in the zone of intense hydrothermal activity depending on the temperature of their formation. Judging by the composition of secondary minerals (smectites, celadonite, zeolites, siliceous minerals), the rocks investigated in the course of this work were washed by groundwater heated to the temperature less than 150°C (Geptner and Sokolova, 1989; Kristmansdottir, 1982). Small accumulations of the bituminous substance were found in some samples of hydrothermally altered rocks. Fine drop-like segregations were detected and studied in a series of polished sections from hydrothermally altered Miocene basalts in the east (Berufjordur) and in the north (Eyjafjordur) of Iceland.

The PAH content was investigated in the following types of rocks: in fresh basalts and in acid and basaltic tephra; in hydrothermal minerals from the zones of fissure mineralization in Miocene plateau-basalts; in the bituminous substance collected from crack walls in hydrothermally altered basalts; in hyaloclastites altered in surface conditions (the present-day weathering crust); and in diluvial-eolian deposits with thin and poorly developed soil horizons. The hydrocarbons were studied from 30 samples of rocks and minerals.

The technique of analysis. Weighed portions (on the average, 20–25 g) of air-dried samples, grinded to the particle size not exceeding 0.25 mm, were taken for

analysis. The extraction of PAH-bearing bituminous substance was performed using *n*-hexane, purified to the absence of luminescence. The bituminous substance was extracted by several portions in glass flasks at room temperature. The end of the extraction was determined by the absence of luminescence in the next (in turn) portion of the extract. The obtained extract was evaporated to 1–2 ml.

The identification and quantitative determination of PAH were accomplished by the Spol'sky luminescence spectroscopy (Alekseeva and Teplitskaya, 1981; Rovinskii *et al.*, 1988). The qualitative and quantitative analyses of PAH were carried out through the comparison of fluorescence spectra for hydrocarbon solutions in *n*-hexane at the boiling temperature of nitrogen (77 K) with the spectra of the SRM 1491 standard solution, representing a mixture of 23 PAH. The selectivity of the analysis was ensured by the application of the "spectral fractionation" method based on the optimum combination of excitation and registration lines for each individual compound or its homologous groups (Alekseeva and Teplitskaya, 1981). The analysis was performed on the "Fluoricord" spectrofluorimeter. The detection limit for intensely luminescent (in the visible region) polycyclic compounds was from 0.01 to 1.00 ng g⁻¹; the detection limit for low-cyclic compounds, luminescent in the near ultraviolet region, was from 1.0 to 10.0 ng g⁻¹. The wavelengths of analytical lines of excitation and fluorescence, mainly used for the PAH identification, are presented in Table 1.

Table 1. Analytical bands in the spectra of excitation (λ_e) and fluorescence (λ_f) used for PAH identification

Polycyclic aromatic hydrocarbons	λ_e , nm	λ_f , nm
<i>Substituted PAH</i>		
homologues of biphenyl and fluorene	278	295–305
homologues of naphthalene-1	289	322
homologues of naphthalene-2	289	325
homologues of phenanthrene	254	348–353
homologues of benzofluorene	313	341–347
homologues of chrysene	269	362–365
homologues of pyrene	345–350	373–382
<i>Unsubstituted PAH</i>		
pyrene	337	372
benzo[a]anthracene	288	384
benzo[a]pyrene	370	403
benzo[ghi]perylene	370	420
perylene	421	447
benzo[k]fluoranthene	310	404
anthanthrene	410	434

DISCUSSION

Polycyclic Aromatic Hydrocarbons in Eruption Products Unaltered by Secondary Processes

Basalts, basaltic tephra, hyaloclastites, and acid tephra from historic eruptions, as well as basaltic hyaloclastites from the volcanic cone of Surtsey Volcano formed during its eruption in 1963–1965, were

selected for the investigation of the PAH content and composition (Tables 2, 3).

All samples of historic eruptions characterize the eastern branch of the modern rift (Fig. 1), in which three zones differing in the composition of volcanic rocks can be distinguished: tholeiites (Krafla, Askja), intermediate alkali basalts (Hekla), and alkali-olivine basalts (Surtsey) (Jakobsson, 1979). Samples of hyaloclastites from Surtsey Volcano were selected in 1972 by A.A. Krasnov, a participant of the USSR Academy of Sciences expedition, and passed them over to us for investigation. The detailed study of hyaloclastites using the optical and scanning electron microscopes showed that the surface of basalt glass fragments was perfectly smooth and devoid of any alteration products.

The hydrocarbons were detected in approximately equal quantities ($35\text{--}62\text{ ng g}^{-1}$) in all investigated lava samples. Homologues of biphenyl and fluorene—hydrocarbons, whose synthesis occurs mainly at high temperatures (above 500°C)—are the predominant compounds in the PAH composition (50% or more of the total amount). The rest of PAH are represented by homologues of naphthalene and, in addition, in quantities equal to about 20% of the total PAH content, by homologues of phenanthrene (in the lava crust) or benzofluorene (tephra of hydroexplosions), detected only in basalts from Surtsey Volcano.

The scatter of PAH content in unaltered acid tephra (Table 3) is fairly wide from 10 to 408 ng g^{-1} . In this case, a clear correlation of the PAH content with the eruption age can be noted. The PAH composition in pumice fragments is close to that in basalts. Homologues of biphenyl and fluorene have not been detected in psammitic basaltic tephra against the background of

Table 2. Distribution of polycyclic aromatic hydrocarbons in unaltered volcanic rocks of Iceland (basalts)

	Northern Iceland			Central Iceland	Southern Iceland	
	Crafla Volcano (1729a)	Crafla Volcano (1729b)	Crafla Volcano (1977)	Askja Volcano (1961)	Surtsey Volcano (1963a)	Surtsey Volcano (1963b)
Polycyclic aromatic hydrocarbons (PAH)	basalt, central part of lava crust	basalt, surficial vitrified part of lava crust	basalt, surficial vitrified part of lava crust	basalt, surface crust	basalt, surficial vitrified part of lava crust	basaltic hyaloclastics
Total content (ng g^{-1})	62	44	37	52	36	35
Distribution (%):						
homologues of biphenyl and fluorene	71	77	62	67	50	51
homologues of naphthalene	23	18	35	25	31	29
homologues of phenanthrene	—	—	3	2	9	—
homologues of benzofluorene	6	—	—	6	—	20
<i>Unsubstituted PAH</i>	—	5	—	—	—	—
pyrene (ng g^{-1})	—	2	—	—	—	—

Note: (1729) sample number and the year of eruption; (—) not detected.

Table 3. Distribution of polycyclic aromatic hydrocarbons in unaltered volcanic rocks of Iceland (tephra)

	Central Iceland	Southern Iceland	
	Hekla Volcano (1875)	Hekla Volcano (1104)	Hekla Volcano (1980)
Polycyclic aromatic hydrocarbons (PAH)	acid tephra, pumice fragment	acid tephra, pumice fragment	psammitic basaltic tephra
Total content (ng g ⁻¹)	50	408	10
Distribution (%):			
homologues of biphenyl and fluorene	52	46	—
homologues of naphthalene	42	27	70
homologues of phenanthrene	4	20	30
homologues of benzofluorene	2	4	—
Unsubstituted PAH	—	3	—
pyrene (ng g ⁻¹)	—	12	—

Note: (1875) sample number and the year of eruption; (—) not detected.

a very low total PAH content (possibly, due to an insufficient sensitivity of the instrument).

The character of PAH distribution in unaltered rocks allows us to believe that these hydrocarbons are syngenetic to basalts and are synthesized directly during the lava flow cooling-off. As to tephra, a later PAH contamination from the surrounding rocks is possible for these rocks due to their high porosity. The equal amount of PAH has been established in recent basaltic lavas and tephra of hydroexplosions on Surtsey Volcano. Hence, different conditions of volcanite formation (a quiet effusion for lavas and hydroexplosions for the tephra formation) have not been reflected on the amount of PAH formed during the eruption.

Polycyclic Aromatic Hydrocarbons in Altered Rocks and Hydrothermal Minerals

Samples of hydrothermally altered basalts and secondary minerals were selected in Miocene basalts of Eastern, Western, and Northwestern Iceland (Tables 4, 5).

In the east of Iceland, samples were taken on the top of Beruffjörður from the sequence of plateau-basalts accumulated synchronously with the formation of the large central-type volcanic complex (Breiddalur Volcano) comprising large quantities of acid subvolcanic intrusions. Basalts are dissected by multiple fissures with the general northward strike toward the central volcanic complex. Cracks and gas cavities in the analyzed rocks are filled with a complex of secondary minerals, basic components of which are (in the sequence of formation): smectites, celadonite, zeolites, and siliceous minerals. During the field investigations, this complex of secondary minerals was followed along the strike of lava beds, whereas nontronites and zeolites play the main role in plateau-basalts upward and downward the section.

The stratiform zonality of secondary mineralization points to the alteration of basalts by heated stratal water. A large amount of siliceous minerals and layered silicates containing a considerable amount of potassium (celadonite) makes it possible to believe that a part of components for the formation of secondary minerals was borrowed by groundwater from acid subvolcanic intrusions. The smectite–celadonite complex of secondary minerals is confined to the zones with maximum permeability, such as fissure–dike swarms, and extends to some distance beyond their boundaries in the cases, when thermal solutions spread laterally within the sequence of plateau-basalts. Beyond the boundaries of fissure–dike swarms, smectites (nontronites) and zeolites dominate in the composition of secondary minerals.

A similar (in the composition and formation conditions) smectite–celadonite complex of secondary minerals has been studied in the north of Iceland in Eyjafjörður and adjacent regions. Here, the secondary mineralization is most intensely developed in the zone of large fissure–dike swarms, which extend to large volcanic centers with acid subvolcanic intrusions. As in the previous case, layered silicates were first to form. Smectites and celadonite compose rims and, in many cases, fill all gas cavities in basalts. Zeolites and siliceous minerals are located in the central parts of cavities and fill small cross cracks.

The total amount of PAH determined in the complex of hydrothermal minerals exceeds that in unaltered rocks by 1–2 orders of magnitude. In this case, various mineral associations differ in the content and composition of PAH.

The largest amount of PAH is detected in the smectite–celadonite complex associating with siliceous minerals and/or zeolites. In 6 samples (Table 4), the average PAH content is about 1000 ng g⁻¹ at the standard deviation 740. The value of scatter was affected by a

Table 4. Distribution of polycyclic aromatic hydrocarbons in secondary minerals of hydrothermally altered basalts (the smectite–celadonite complex)

	Northern Iceland	Northwestern Iceland	Western Iceland	Eastern Iceland		
	Nupä River valley	Kollafjordur	Nordurä River valley	Berufjordur		
Polycyclic aromatic hydrocarbons (PAH)	smectites, celadonite (965/19)	smectites, celadonite (9732)	celadonite + smectites (9728)	secondary minerals from a veinlet: smectite, celadonite, chalcedony, zeolites, pyrite, (9725/1)	secondary minerals from a gas cavity: smectite, celadonite (9725/2)	basalt + secondary minerals (smectites, celadonite, zeolites, chalcedony), drops of bituminous substance in gas cavities (9725/3)
Total content (ng g ⁻¹)	672	922	2543	1009	1314	135
Distribution (%):						
homologues of biphenyl and fluorene	32	41	0	39	16	47
homologues of naphthalene	58	50	78	16	69	41
homologues of phenanthrene	7	5	18	25	11	7
homologues of benzofluorene	2	3	3	6	2	3
homologues of chrysene	–	–	–	4	–	–
homologues of pyrene	–	–	–	10	1	–
Unsubstituted PAH	1	1	1	–	1	2
pyrene (ng g ⁻¹)	5	5	19	–	6	2

Note: (9732) sample number; (–) not detected.

relatively low (135 ng g⁻¹) PAH content in Sample 9725/3, in which the complex of secondary minerals turned out to be “diluted” by fragments of host basalt in the process of its preparation for analysis. The PAH contents in other samples vary from 672 to 2543 ng g⁻¹. The PAH composition in minerals of the smectite–celadonite association is fairly variable and depends not so much on the region of sampling as, probably, on the conditions of mineral formation, i.e., the intensity of circulation and temperature of hydrothermal solutions. It is clearly seen on the composition of PAH from samples taken in Berufjordur (Eastern Iceland). Here, homologues of fluorene and biphenyl and homologues of naphthalene are present in basalts, comprising secondary minerals in amygdules, approximately in equal fractions (47 and 41%, respectively). The rest of PAH are homologues of phenanthrene and benzofluorene (7 and 3%, respectively) and pyrene (2%). In secondary minerals deposited in a large gas cavity, the total PAH content is higher by a factor of 10; homologues of naphthalene sharply dominate (69%). The rest of PAH are homologues of biphenyl and fluorene and homologues of phenanthrene (16 and 11%, respectively). Pyrene constitutes 1% of the total PAH component. In secondary minerals taken from a cross crack, at the same high total content of PAH, homologues of biphenyl and fluorene (39%) and homologues of phenanthrene (25%) dominate. Homologues of

pyrene appear in a noticeable amount (10%), but unsubstituted PAH are absent.

The presence of fluorene and biphenyl homologues is common for the majority of samples of the smectite–celadonite association (16–47% of the total PAH content in 5 samples out of 6).

In the nontronite–zeolite complex of minerals, the total PAH content varies from 25 to 822 ng g⁻¹ (Table 5). On the average, it is equal to about 400 ng g⁻¹ for 6 samples, which is by a factor of 2.5 less than in the smectite–celadonite complex. The PAH composition differs from that described above. Homologues of fluorene and biphenyl were encountered only in half of the samples (19–46%). A relatively noticeable amount of chrysene homologues is present in samples from the Skál-mardalur and Berufjordur regions (38 and 9%, respectively).

Of all investigated secondary minerals, siderite contains the largest amount of PAH (2326 ng g⁻¹) consisting of naphthalene homologues to the extent of 83%.

It is possible that a different amount of PAH in secondary minerals reflects the conditions of mineral formation: the paleotemperature of groundwater, intensity of circulation, and relative time of formation of secondary minerals. The smectite–celadonite association, as mentioned above, was formed predominantly in the areas of development of large fissure swarms and, con-

Table 5. Distribution of polycyclic aromatic hydrocarbons in secondary minerals of hydrothermally altered basalts (the smectite-zeolite complex)

	Northern Iceland	Northwest- ern Iceland	Western Iceland			Eastern Iceland	
	Eyjafjördur	Skál- mardalur	Nordurá River valley			Berufjördur	
Polycyclic aromatic hydrocarbons (PAH)	basalt + secondary minerals (smectites, zeolites), drops of bituminous substance in gas cavities (963/1)	nontronite + zeolites (9731)	siderite + nontronite (9727a)	nontronite (9727b)	nontronite (9729)	nontronite, some zeolites (9721)	zeolite (9723)
Total content (ng g ⁻¹)	233	625	2325	822	644	25	94
Distribution (%):							
homologues of biphenyl and fluorene	46	19	—	—	36	—	—
homologues of naphthalene	36	36	83	71	51	100	39
homologues of phenanthrene	15	4	9	26	8	—	32
homologues of benzofluorene	2	2	—	—	4	—	14
homologues of chrysene	—	38	3	—	—	—	9
homologues of pyrene	—	—	1	—	—	—	—
Unsubstituted PAH	1	1	4	3	1	—	6
pyrene (ng g ⁻¹)	3	4	100	23	6	—	6

Note: (9731) sample number; (—) not detected.

sequently, intense circulation, and possibly a higher temperature of groundwater. In all of the studied samples, clay minerals were formed earlier than others. Among layered silicates, the K-bearing smectite-celadonite complex builds earlier (evidently higher-temperature) zones replaced by smectites, among which Fe-rich varieties (nontronites) prevail. It is important to emphasize that siderite segregations, containing the largest amount of PAH among secondary minerals, were also the first to form on the walls of gas cavities in the porous part of basaltic lava flows.

BITUMINOUS SUBSTANCES

Fine spherical black drops of the bituminous substance (the diameter of drops is less than 1 mm) were located on the walls of cracks cross-cutting amygdulites and secondary mineral. In polished sections, they look like black and darkbrown, weakly translucent tiny (fractions of mm) drop-like and spherical formations located within the field of bright-green clay minerals. In some cases, they are confined to small cracks dissecting clay mineral segregations (Fig. 2). The analysis of interrelations between secondary minerals and bitumen accumulations has made it possible to determine a relative timing of the latter. Bitumen segregations were formed simultaneously with clay minerals or immediately after them.

The total PAH content in the bituminous substance is 946 ng g⁻¹. The set of substituted PAH, typical of the bituminous substance from the regions of intense hydrothermal activity, such as homologues of naphthalene, phenanthrene, benzofluorene, and pyrene, was detected in the bituminous substance. Unsubstituted PAH are, as a rule, detected in such samples in very insignificant quantities or are not detected at all (possibly, due to the camouflage of the spectrum by essentially prevailing substituted structures).

Table 6 presents the comparison of PAH distribution in the bituminous substance from basalts of Iceland with counterparts in other regions of the modern hydrothermal activity: Uzon Volcano caldera in Kamchatka (Pikovskii *et al.*, 1987) and Guaymas Basin in the Gulf of California (Pikovskii *et al.*, 1996).

It is evident that the PAH distribution in the bituminous substance of Iceland, taken out of a small crack in basalts, fits completely in the scatter of PAH values that had been established for these hydrocarbons in products of the modern hydrothermal activity in a number of other volcanic regions.

THE ZONE OF WEATHERING OF HYALOCLASTITES AND ELUVIAL-DILUVIAL DEPOSITS

In order to reveal the content and distribution of PAH in surficial loose deposits, we investigated basaltic

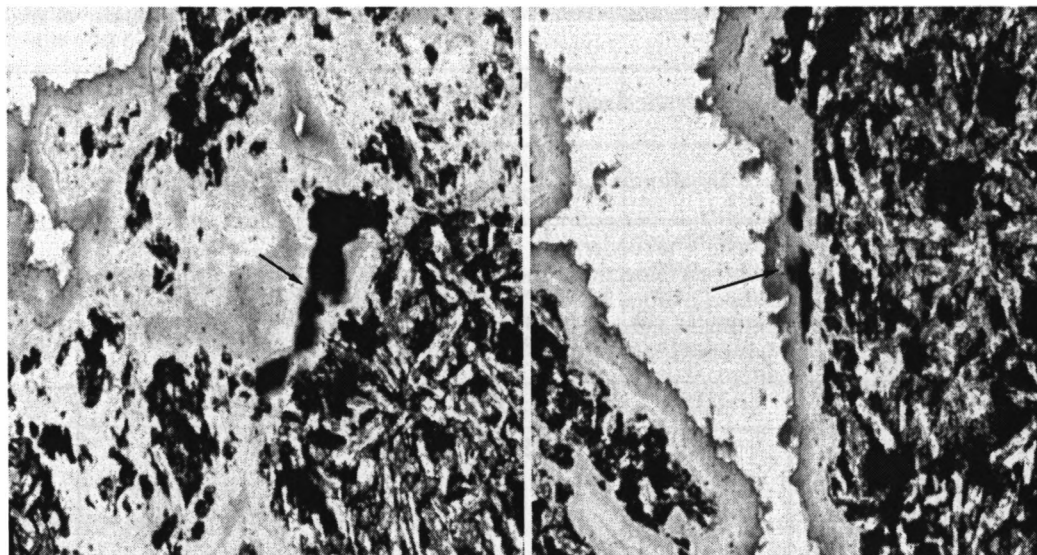


Fig. 2. Character of the bituminous substance segregation (the arrow) in hydrothermally altered basalts. The gray background represents clay minerals; polished section, magn. 100; Sample 963-1.

hyaloclastites from the modern zone of weathering in the sequence of Pleistocene subglacial eruptions outcropping on the slope of the Kälftindar ridge, as well as eolian-diluvian deposits located on the slope of the Fnjoska River valley and on the surface of Holocene lava flow in the Skjaulfandafljot River valley, westward of the Godafoss waterfall (Table 6).

Pleistocene hyaloclastites were formed in an intraglaciac lake in the process of hydroexplosions at the

instant when the magmatic melt came into contact with water. In the weathering zone, hyaloclastites are altered and partially substituted by palagonite imparting the yellow and brick-brown color to the rock. The thickness of weathering zone depends on the topographic features and the presence of fissured zones. On low-angle slopes of the ridge, the thickness of altered rocks is about 1 m, whereas on steep slopes, it does not exceed a few centimeters or is absent altogether.

Table 6. Distribution of PAH in the bituminous substance from plateau-basalts of Iceland and from other regions of modern hydrothermal activity

Polycyclic aromatic hydrocarbons (% of the total content in the bituminous substance)	Iceland, drops of the bituminous substance from a small crack in basalts	Uzon Volcano caldera (liquid petroleum segregation at the groundwater surface)		Guaymas Basin (a sulfide edifice at the "black smoker")	
Sample no.		189	7A/84	1524	1583
<i>Substituted PAH</i>					
homologues of naphthalene	20.6	18.8	43.1	15.5	12.3
homologues of phenanthrene	42.3	67.1	24.0	25.0	9.9
homologues of benzofluorene	8.0	4.2	11.7	8.5	6.0
homologues of chrysene	—	—	4.9	2.7	—
homologues of pyrene	29.1	8.6	13.2	45.1	30.9
<i>Unsubstituted PAH</i>					
pyrene	—	—	1.5	—	32.4
benzo[a]anthracene	—	—	—	—	1.5
benzo[a]pyrene	—	—	0.5	2.4	1.1
benzo[ghi]perylene	—	—	—	—	—
perylene	—	1.2	1.0	0.4	5.8

Note: Traces of biphenyl and fluorene homologues are observed in all samples.

Table 7. Distribution of polycyclic aromatic hydrocarbons in the weathering zone of hyaloclastites, in eolian–diluvial deposits, and in deposits of a submarine hot spring

	Kälfstindar Ridge	Godafoss waterfall region	Western slope of the Fnjoska River valley	Northern Iceland, Eyjafjördur
Polycyclic aromatic hydrocarbons (PAH)	basaltic hyaloclastites of the modern weathering zone (97–50)	loose cover on the lava flow (77280)	loose cover on fluvioglacial deposits (82521)	deposits of a submarine hot spring (E-2)
Total content (ng g ⁻¹)	515	458	318	1366
Distribution (%):				
homologues of biphenyl and fluorene	61	61	78	25
homologues of naphthalene	31	31	19	65
homologues of phenanthrene	3	2	–	4
homologues of benzofluorene	4	3	1	4
homologues of chrysene	–	2	2	–
homologues of pyrene	1	–	–	1
Unsubstituted PAH	1	1	–	1
pyrene (ng g ⁻¹)	4	5	–	11
benzo(a)anthracene (ng g ⁻¹)	–	–	–	5

Note: (77280) sample number; (–) not detected.

Loose sediments forming the sheet on deposits of different age, genesis, and geomorphological position are composed of eolian deposits with traces of sliding on steep slopes. The thickness of these deposits varies from 0.5 to 1.5 m. The deposits investigated by the authors are located in the north of Iceland. The sheet material contains products of redeposition of glacial and fluvioglacial deposits and a large amount of volcanic explosion products. Basalt glass in the composition of the latter plays the main role. Sheet deposits include layers of acid and basaltic ashes, and some horizons are rich in weakly decomposed vegetable remains, mainly the remains of herbaceous vegetation. Tephrochronological investigations have made it possible to date these deposits (Thorarinsson *et al.*, 1959). Samples were taken from sediments of approximately the same age located on the river valley slope (82521) and on the surface of Holocene lava flow (77280) (Fig. 1). The horizons, from which the analyzed samples were taken, lie in the upper part of sheet deposits. They are younger than the acid ash of Hekla Volcano deposited 2800 year ago, and older than ash of Hekla Volcano erupted in 1104. Hence, the analyzed sediments were formed prior to the period of populating of the island.

In the Fnjoska River valley, loose sediments lie on Miocene plateau-basalts that make up a flexure, whose lowered side is dissected by multiple fractures and dikes. Plateau-basalts in the Skjalfandafljot River valley, overlain by the lava flow and eolian sediments, are also dissected by multiple fractures and dikes (Zverev *et al.*, 1980).

The PAH content in the studied samples of hyaloclastites from the weathering zone and loose sheet is of the same order: from 318 to 515 ng g⁻¹. The hydrocarbons consist of homologues of biphenyl and fluorene to the extent of 60–80%. Homologous of naphthalene constitute from 20 to 30% of the total PAH content. In addition, homologues of phenanthrene, benzofluorene, and chrysene are detected in the studied samples (*n*% of the total PAH content). A certain amount of unsubstituted PAH represented by pyrene are present in hyaloclastites from the weathering zone and loose sediments on the lava cover. In addition, a fluorescence band of unsubstituted biphenyl is distinctly pronounced in loose sediments.

In comparison with fresh modern basaltic lavas and hyaloclastites of Surtsey Volcano, Pleistocene hyaloclastites altered in the surface conditions contain PAH in quantities larger by more than one order of magnitude. Eolian sheet sediments are close to them in the PAH content. One of the reasons for this can be the fact that, in both cases, products of basaltic tephra alteration (hyaloclastics) consisting chiefly of palagonite, which is distinguished by extremely high porosity and sorption ability, are similar.

SEDIMENTS OF SUBMARINE HOT SPRING

The submarine spring found on the fiord bottom in the north of Iceland (Eyjafjördur) represents an example of the present-day submarine postvolcanic hydrothermal activity. Sample E-2 from a submarine thermal edifice was handed to A.P. Geptner for investigation by Dr. Jakob Kristjansson (Institute of Biology, University

of Iceland) in the summer of 1997. It would be of interest to consider the PAH distribution in sediments of this spring. The PAH content in the analyzed sample is presented in Table 7.

The total PAH content is fairly high here ($>1000 \text{ ng g}^{-1}$). Homologues of naphthalene (65%) and homologues of biphenyl and fluorene (25%) constitute 90% of PAH. Homologues of phenanthrene, benzo[fluorene], and pyrene are present in the amount of a few percent of the total PAH. Pyrene and benzo[a]anthracene are noted among unsubstituted structures. In this sample, two groups can be clearly distinguished among naphthalenes. One of these groups with the band 325 nm corresponds to the luminescence of di-substituted and tri-substituted homologues of naphthalene. This group is met in all of the investigated samples. The other group with the band 322 nm corresponds to the luminescence of naphthalene, acenaphthene, or some other similar PAH. Apart from the given sample, this group of naphthalene homologues was met in PAH associations from hydrothermal minerals: in the smectite–celadonite complex from the Nupá River valley (965/19), and from the regions of Kollafjörður (9732) and Berufjörður (9725/2), as well as in two samples of nontronite from the region of Skálmdalur (9731) and from the Nordurá River valley (9729). In other samples, a similar group of naphthalenes was observed in an insignificant amount in the loose sheet in the Fnjoskan River valley (82521).

On the whole, in terms of content and composition, hydrocarbons encountered in sediments of the submarine hot spring are closest to those in hydrothermal minerals (especially the smectite–celadonite complex) from altered basalts.

CONCLUSION

The carried out investigation has demonstrated that hydrocarbons in volcanic rocks of Iceland do not represent any exotic or accidental phenomenon but are an obvious result of the volcanic and postvolcanic hydrothermal activity. The investigation of samples from various types of rock and minerals taken from different geological structures of Iceland has shown the presence of dispersed bituminous substances containing polycyclic aromatic hydrocarbons in them. Three genetic groups of PAH can be clearly distinguished by their composition and quantitative content: (1) hydrocarbons syngenetic to basalts formed from simple compounds of carbon and hydrogen during the solidification of lava; (2) hydrocarbons circulating in postvolcanic hydrothermal solutions and precipitating from these solutions together with various complexes of hydrothermal minerals; and (3) hydrocarbons incorporated into a composition of carbonaceous segregations of the asphalt and asphaltite types in cracks and cavities of altered basalts.

The origin of PAH detected in sheet sediments and in the weathering zone of Pleistocene hyaloclastites is not clear. Probably a high porosity of these rocks and the presence of basalt alteration products (very porous palagonite) favored the contamination of PAH from the environment. Volcanic eruptions in the nearest neighborhood could be one of the sources of PAH. The possibility of hydrocarbon supply from the Earth's interior in zones with increased permeability, which can be represented by zones of fractures and fissure–dike swarms, must not be ruled out either.

It is well seen from the presented data that hydrothermally altered basalts and secondary minerals are distinguished by a high PAH content, as compared to fresh (unaffected by hydrothermal alterations) volcanites of the basaltic and acid composition. In secondary minerals, the PAH content was found to be by a factor of 7–10 higher than in hydrothermally altered host basalts.

Hydrocarbons, including PAH, are natural components of hydrothermal solutions at all stages of their evolution. Aggregation of hydrocarbons into high-molecular polycyclic compounds of the type of resins and asphaltenes and their micro- and macrosegregations in the form of asphalts, asphaltites, and other carbonaceous formations occur at the last (low-temperature) stage of the hydrothermal process crowning its evolution (Florovskaya *et al.*, 1986; Pikovskii, 1993). Therefore, all three genetic groups of PAH can be considered as products, whose appearance is connected with the development of naturally conjugated volcanic and postvolcanic processes.

Sources of carbon in this process can be different, including the borrowing from carbonaceous sedimentary rocks. Unfortunately, there are no reliable "markers" allowing us to distinguish endogenic sources of carbon from exogenic ones. The isotope analysis of carbon cannot serve here as a reliable criterion due to a wide differentiation and fractionation of isotopes. For Iceland, where sedimentary carbonaceous rocks play no essential role in a geological section, the sedimentary source for the formation of hydrocarbons detected in volcanogenic rocks of different ages and structural positions, as well as in hydrothermal formations, seems unlikely.

The data on the ratio of methane and hydrogen contents in gases of fumaroles and hydrotherms of Iceland, analyzed by the authors, point to an endogenic source of hydrocarbons. The available materials characterize high-temperature hydrothermal systems of the western (Reykjanes–Svartsengi, Krisuvik, Nejavellir–Hveragerdi) and eastern (Torfajökull, Namafjall–Krafla) rift zones (Arnorsson, 1987; Arnorsson *et al.*, 1987; Kristmannsdottir, 1991). All of the mentioned hydrothermal systems are situated within the boundaries of active volcanic regions in zones of hydrogen therms, in which the steam and water jets contain an amount of free hydrogen (Kononov, 1983).

The rest of the considered hydrothermal systems are spatially connected with the distribution of acid rocks (rhyolites), except for the Reykjanes–Svartsengi and Krisuvik hydrothermal systems that do not display any definite relation to acid volcanic rocks. Especially large massifs of rhyolites and dacites are known in the zone of the Torfajökull thermal system activity (Arnorsson *et al.*, 1987). The direct correlation between the contents of hydrogen and methane is clearly exhibited in fumaroles gases of this thermal system. The comparison of data on the Krafla thermal system, which represents a large caldera, with rhyolite bodies exposed inside and on edges (acid ash precipitated during the caldera formation is known in the adjoining territories), the Nesjavellir system (with outcrops of rhyolites), and the Svartsengi system (without rhyolites) reveals a definite connection between acid rocks in the thermal system field versus a relative increase and direct correlation of hydrogen and methane in fumarole gases.

Based on the fact that the composition and distribution of hydrocarbons in volcanic and hydrothermal formations result from physicochemical conditions of the consolidation of volcanites and secondary mineral formation rather than from local features of the geological structure, one should assume that hydrocarbons in the volcanic and postvolcanic processes are connected with the endogenic supply of carbon and hydrogen.

Undertaking this work, the authors pursued the goal to attract the attention of investigators to the problem of the origin of hydrocarbons in volcanic formations of Iceland, thinking that, apart from a purely scientific significance, such investigations may be of a substantial practical significance as well, for example, for elucidating whether the formation of hydrocarbon raw material resources is possible in volcanic regions.

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Mineralogy of Phosphatic Sand from the Namibian Shelf

G. N. Baturin* and V. T. Dubinchuk**

* Shirshov Institute of Oceanology, Russian Academy of Sciences, Nakhimovskii pr. 36, Moscow, 117851 Russia

** All-Russia Institute of Mineral Resources, Staromonetnyi per. 29, Moscow, 109017 Russia

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Abstract—The mineralogy of phosphatic sand from the outer Namibian shelf was studied on phosphatic grains picked out of 2–1 and 0.25–0.1 mm fractions. Grains were studied under scanning and transmission electron microscopes coupled with microdiffraction. Grains consist of colloform, globular, and crystalline phosphate intermixed in various proportions, with minor admixtures of bone debris and fish scales. Nonphosphatic material consists of biogenic silica (diatom remains), biogenic carbonate (coccolith and foraminifera remains), illite, globular and finely dispersed pyrite, and barite. Furthermore, rare inclusions of wüstite, ferroxyhyte, coffinite, monazite, native silver, sternbergite, cellaite, and shercolite were also found. The structure and mineral composition of grains are similar to those of recent phosphatic accretions from diatomaceous ooze of the inner Namibian shelf that may prove their similar origin.

INTRODUCTION

Phosphatic sand on the outer Namibian shelf are common in areas between 24° and 26° S. They form up to 2-m-thick deposit lying at a depth of 180 to 230 m. The character and extent of deposit are comparable to those of phosphatic sand layers of Georgia and North Carolina described by Riggs *et al.* (1985) and Riggs and Manheim (1988).

The discovery of this deposit is related to expeditions of research vessels belonging to the Atlantic Branch of the Research Institute of Fisheries and Oceanography of the former Soviet Union carried out beginning from early 1960s, when a number of grab sediment samples enriched in phosphatic grains was recovered (Senin, 1968, 1970). Subsequently, this area was investigated in more detail, followed by the discovery and mapping of a phosphatic ore field and evaluation of its potential resources as being about 4 Gt of P₂O₅ (Bremner, 1992). According to Sr isotope dating, phosphatic grains formed during the Pliocene to Pleistocene time and might be considered as the youngest pelletal phosphorites yet to be known (McArthur *et al.*, 1990).

General information concerning the structure and composition of lithified phosphatic grains from this area is published in a number of works (Baturin, 1978; Baturin *et al.*, 1998a; Bremner, 1980; Bremner and Rogers, 1990; Emel'yanov, 1973; Senin, 1970). However, their mineral composition was not a subject of special investigation. The present work aims at filling this gap.

MATERIALS AND METHODS

Material for this work was recovered during the 4th cruise of R/V *Professor Logachev* (1992) owing to the

efforts and participation of J.M. Bremner and P.D. Dillon from Cape Town University. The sediment sample weighing about 1 t was recovered in the central part of deposit (25°15.90' S, 14°04.01' E, depth 199 m) by means of video-monitored Preussag grab for further combined investigations in scientific and industrial organizations of Republic of South Africa and Russia. Part of this sample was placed at our disposal by the chief geologist of the cruise O.V. Kolosov.

Granulometric and bulk mineralogical compositions of this sample were studied by traditional granulometric and microscopic methods in the State Institute of Chemical Raw Materials. Chemical composition of size fractions was determined by chemical and atomic absorption methods in the Shirshov Institute of Oceanology of Russian Academy of Sciences, with the exception of bulk sulfur and fluorine analyzed in the chemical laboratory of Geological Institute of Strasbourg University.

The structure and mineral composition of grains were studied under transmission and scanning electron microscopes coupled with microdiffraction in the All-Russia Institute of Mineral Resources. Several samples were additionally studied by the first author, along with E.A. Zhegallo, under scanning electron microscope coupled with microprobe in the Institute of Paleontology, Russian Academy of Sciences.

Phosphatic grains were hand-picked from fractions 2–1 and 0.25–0.1 mm that account, especially the latter fraction, for about a half of phosphatic matter of the bulk sample. Grain surfaces were studied along with fresh fractures. Part of the grains from the 0.25–0.1 mm fraction were subject to short-time etching by 10% HCl, which aimed to reveal more details of their structure.

Table 1. Granulometric and Mineralogical Composition of Phosphatic Sand

Granulometric fractions, mm	Concentration of fractions, %	Composition of fractions, %				
		phosphate	carbonate	quartz	illite and glauconite	others
>2	34.3	28.3	67.6	—	0.7	3.7
–2 + 1	6.8	62	31	—	3	4
–1 + 0.5	3.4	72	21.5	Traces	3.5	3
–0.5 + 0.25	15.1	74	25	0.5	—	0.5
–0.25 + 0.15	23.5	80	7	5	4	4
–0.15 + 0.10	9.0	75	7	7	6	5
<–0.10	7.9	17.5	33.3	20	17	9
Bulk composition	100	54.0	35.0	2.5	5.0	3.5*

* Pyrite 2%, iron hydroxides 0.5%, others 1.0%.

Samples for the transmitting electron microscope were powdered by carbon, and those for transmitting electron microscope were powdered by gold.

GENERAL CHARACTERISTIC OF PHOSPHATIC SAND

The bulk sample consists of 66% sand and 34% gravel fractions. The latter fraction is dominated by shell material consisting of intact and fragmented pelecypod and rarer gastropod shells filled with poorly cemented sand. The gravel fraction includes fragmented fish and marine mammalian bones along with dense phosphatic nodules having glazed or matted surface. In the whole, this fraction consists of 67.6% calcareous and 28.2% phosphatic material.

The composition of sand is dominated by 0.5–0.25, 0.25–0.15, and 0.15–0.1 mm fractions (47.6% of bulk sediment) containing 74–80% phosphate, 7–25% carbonate, and minor amounts of quartz, clay minerals, and pyrite. The fine fraction (<–0.10 mm) consists of carbonate (33%), quartz (20%), clay minerals (17%), and phosphate (17.5%) (Table 1).

The chemical composition of fractions from which grains were picked up is presented in Table 2 along with compositions of fine silt and bulk sediment given for comparison.

Coarse- and fine sand fractions contain 19.7 and 24.84% P_2O_5 , whereas individual phosphatic grains picked up from coarse sand fraction are essentially enriched in P_2O_5 up to 31.36% (on the average) that is apparently typical of all grains relatively devoid of non-phosphatic admixtures. Coarse sand and fine sand fractions are characterized by monotonous MgO (1.22–1.33%) and Na_2O (1.21–1.26%) concentrations, whereas fine fraction is enriched relative to the coarse fraction in SiO_2 (6.2 and 3.05%), Al_2O_3 (1.2 and 0.51%), and Fe_2O_3 (3.6 and 1.3%), but depleted in carbonate (CO_2 6.8 and 16.9%).

As compared to sand fractions, the coarse silt fraction is depleted in P_2O_5 (15.2%) and enriched nearly up to 40% in SiO_2 . Phosphatic grains that are the major component of phosphatic fractions have rounded or sometimes oval and angular form, with smooth surface (Fig. 1). They are characterized by a hardness of 4–5 (according to the Moh's scale) and a specific weight of 2.5–2.9.

STRUCTURE AND MINERAL COMPOSITION OF GRAINS

Grains are built mostly of diagenetic calcium phosphate with inclusions of biogenic phosphatic material and admixtures of nonphosphatic matter.

Table 2. Chemical composition of fractions, %

Component	Fractions, mm			Bulk sample
	2–1	0.25–0.1	0.1–0.05	
P_2O_5	19.7	25.50	10.91	17.3
CuO	51.4	44.1	25.7	44.2
MgO	1.33	1.22	1.35	0.6
Na_2O	1.21	1.26	0.92	—
SiO_2	3.05	6.2	39.9	3.7
Al_2O_3	0.51	1.2	2.8	3.0
Fe_2O_3	1.08	3.6	4.8	2.3
BaO	—	0.02	0.01	—
CO_2	16.43	6.8	8.78	18.0
C_{org}	0.81	1.30	1.03	—
S_{tot}	—	2.69	0.95	1.52
F	1.43	2.91	1.17	1.9
U	—	0.010	0.007	—

Note: (–) not analyzed.

Calcium phosphate is represented by colloform, ultramicrogranular, globular, and crystalline varieties.

Colloform phosphate looks like unstructured mass which reveals no crystalline features even under greatest available magnifications, up to 30000 times (Fig. 2a). Ultramicrogranular phosphate appears as densely packed agglomerations of particles of various size and shape in some parts of grains (Fig. 2b).

Globular phosphate is represented by globular and botryoidal bodies with smooth or bulbous surface ranging from approximately one to some tens of micrometers in a cross section. Some globules are somewhat flattened, with holes inside (Fig. 2c), whereas others are covered by an envelope filled with ultramicrogranular matter seen after etching by HCl (Fig. 2d).

Crystalline phosphate has the form of blocks or prismatic aggregates (Fig. 2e), elongated micrometer-sized particles (Fig. 2f), and crystallized globules. Elongated particles have a rod-shaped or dumbbell-shaped appearance and are predominantly formed where free space is available, in particular, on the surface of colloform phosphate and in voids left after dissolution of biogenic matter. According to the microdiffraction pattern, phosphate is represented by apatite with reflections $d_1 = 8.08 \text{ \AA}$ ($1\bar{1}100$), $d_2 = 3.02 \text{ \AA}$ ($21\bar{3}0$), and $d_3 = 2.69 \text{ \AA}$ ($30\bar{3}0$).

Much of the grains contain inclusions of primary phosphatic biogenic material such as fragments of fish scales and bones, where inner channels are partly filled with diagenetic phosphate.

Calcareous material is present in the form of intact or fragmented coccolithoforidae and rarer foraminifera. According to determinations by T.A. Khusid (Institute of Oceanology, Russian Academy of Sciences), coccoliths belong to *Emiliania huxleyi* (Lohm) Hey, Mokler. Under greater magnifications, separate calcite microcrystals of possible biogenic origin (coccolith fragments) are seen in the phosphatic matrix as well (Figs. 3a–3c).

Opal is represented by diatom remains that are mostly phosphatized (Fig. 3d). Intact diatom frustules are not found, whereas voids left after their dissolution are common. Quartz of seemingly terrigenous origin is encountered as separate minute grains.

Layered aluminosilicates, predominantly illite, are common and are seen in most mounts in the form of platelets with ragged edges, films, and irregular aggregates (Figs. 4a, 5a). Microdiffraction pattern of this mineral is monocrystalline. The crystallographic direction of reverse lattice determined by electron beam is $[001]$.

Pyrite is an ubiquitous component of grains found mostly as dispersed micrometer-sized inclusions of cubic, cuboctahedral, or irregular form or rarer fram-boids up to 20 μm in diameter (Figs. 4b, 4c).

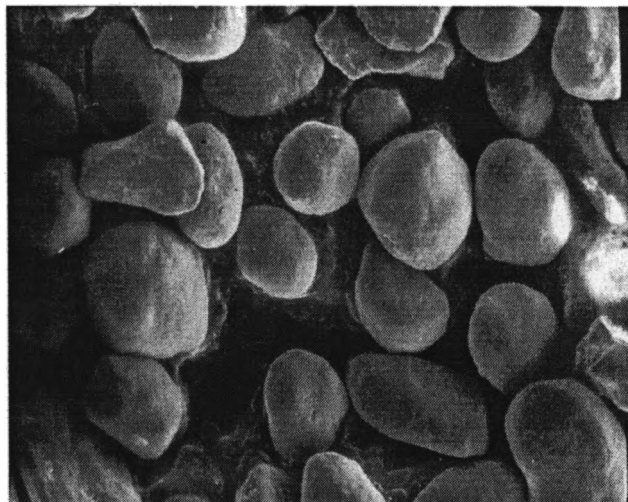


Fig. 1. Phosphatic grains from 0.25–0.1 mm fraction.

Barite is relatively common in the form of platelets, irregular aggregates, and acicular crystallites dispersed in phosphatic matrix (Figs. 3c, 5a, 5b). The microdiffraction pattern of barite is debay-type and microcrystalline, with diffraction maxima $d_{110} = 3.99 \text{ \AA}$, $d_{111} = 3.81 \text{ \AA}$, and their combinations.

Gypsum is found in the form of rare inclusions of prismatic microcrystallites up to 1 μm long in association with barite (Fig. 3c).

Feroxyhyte found in several mounts is represented by two morphological types, namely felted aggregates and replacement of organic remains up to 1 to 1.5 μm in size reminding actinomicetae spores. In the first case, feroxyhyte overgrows the barite crystal, in the second case it replaces organic remains embedded in the phosphatic matrix (Figs. 5b, 5c). Microdiffraction pattern of barite reveals a debay-type pattern with reverse lattice indices 100, 102, 110, and so on; index 101 is absent probably due to the defective nature of mineral structure.

Wüstite is found in only one mount where it replaces worm-like organic remains resembling filamentous, presumably sulfate-reducing bacteria (Fig. 5d). The microdiffraction pattern of wüstite is monocrystalline. The crystallographic direction determined by electron beam is $[101]$. Diffraction spacings of crystalline lattice are 2.43, 2.06, 1.60, 1.45, and 1.27 $\text{\AA}$.

Monazite is found twice. In the first case, it has a tablet form in association with finely dispersed elongated aggregate, whereas in the second case, it is represented by rhombic crystallite about one micrometer long (Figs. 6a, 6b). The monocrystalline microdiffraction pattern of monazite reveals reflections $d_{101} = 5.30$, $d_{111} = 4.20$, and $d_{210} = 3.09 \text{ \AA}$. The crystallographic direction determined by electron beam is $[120]$. Diffraction spacings of crystalline lattice are 5.0, 4.28, 3.0, 2.64, and 2.25 $\text{\AA}$.

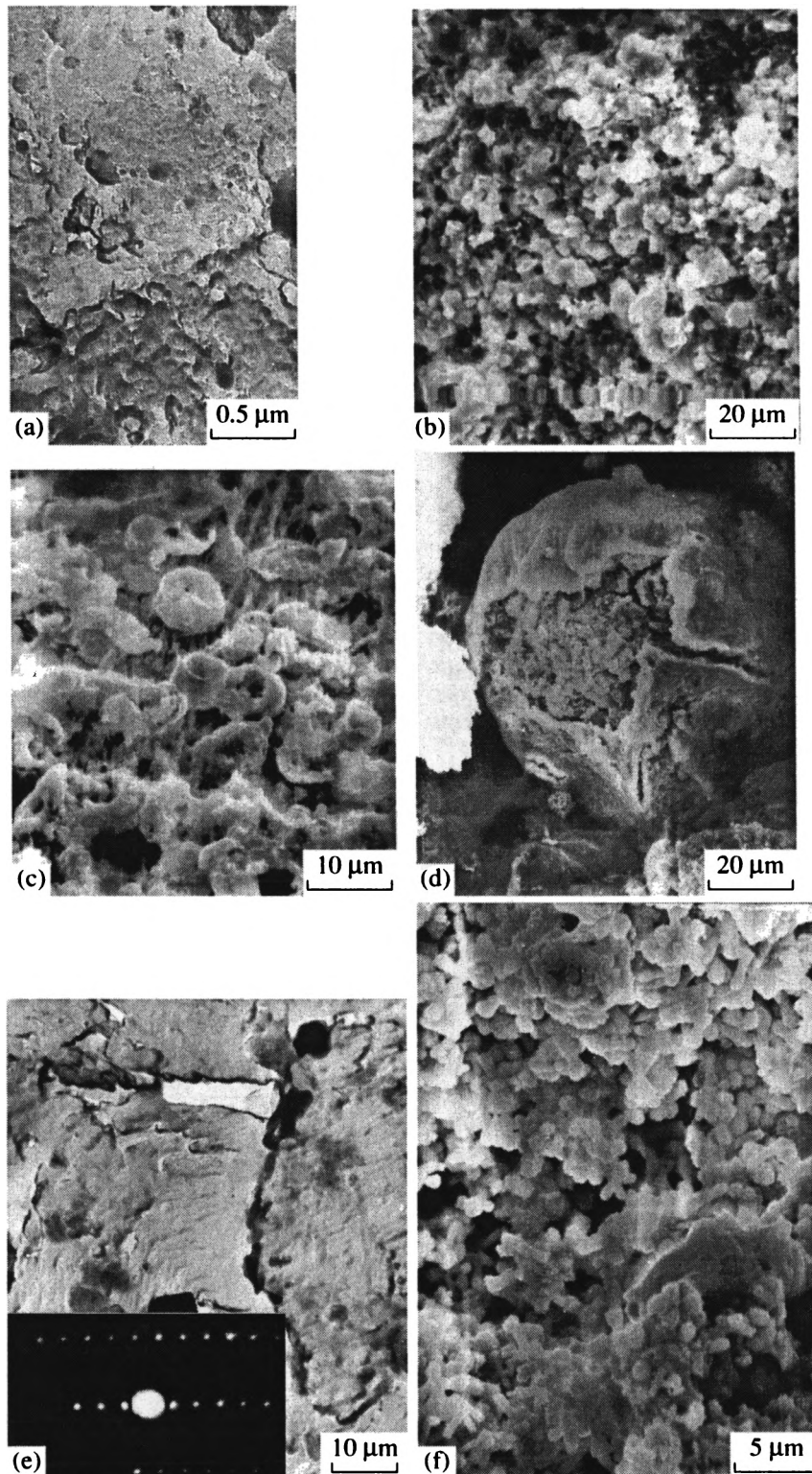


Fig. 2. Morphology of phosphatic matter. (a) Colloform phosphate (2–1-mm-fraction grains); (b) ultramicrogranular phosphate (0.25–0.1 mm fraction); (c) globular phosphate (2–1 mm fraction); (d) globule with envelope filled with ultramicrogranular mass (0.25–0.1 mm fraction); (e) pseudoprysmatic phosphate (in the center) and its microdiffraction pattern; (f) aggregate of elongated micrometer-sized crystallites (2–1 mm fraction).

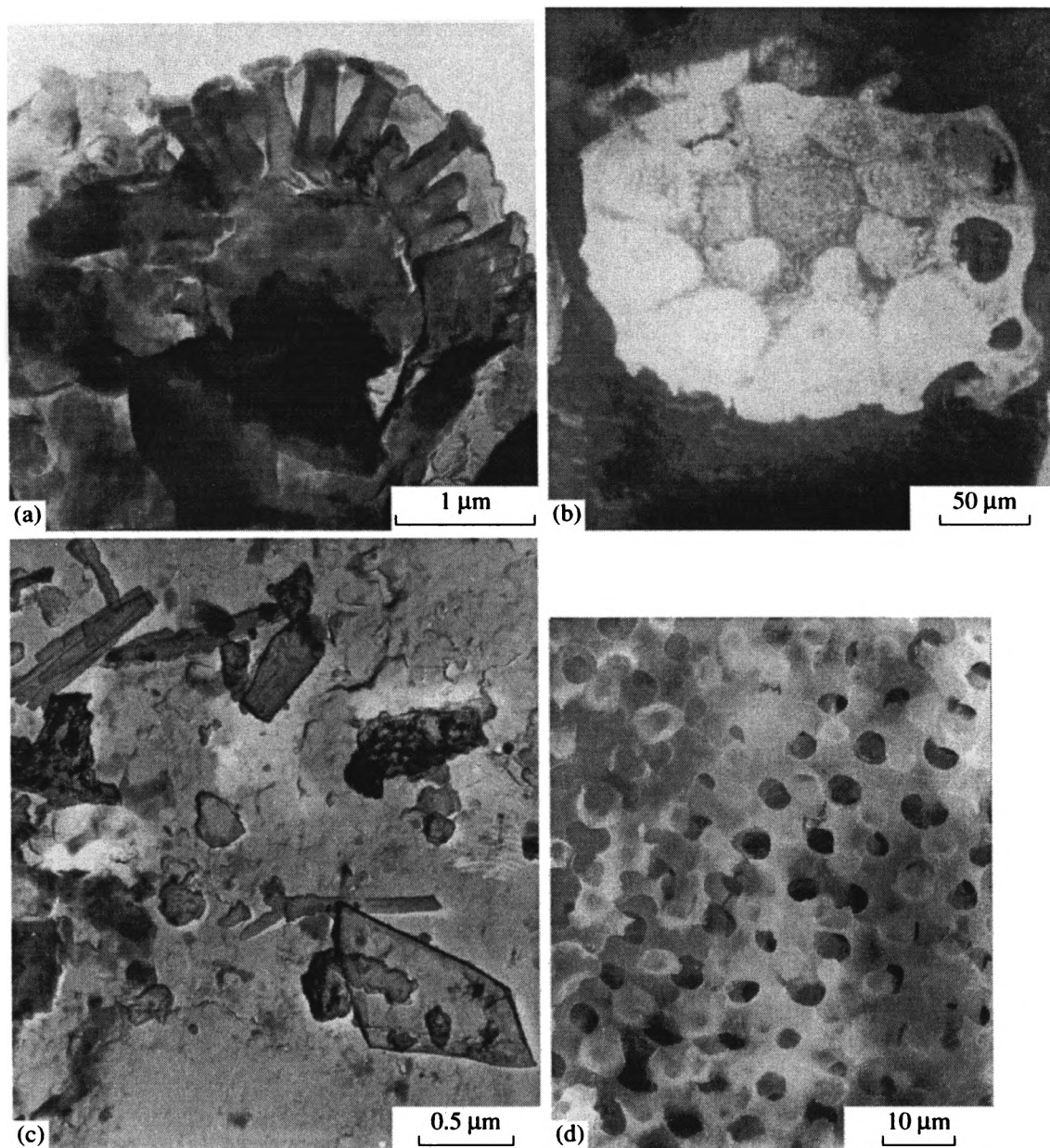


Fig. 3. Carbonate material in grains. (a) Remains of coccolith *Emiliana huxleyi* (Lohm) Hey Mokler in a large grain; (b) bottom foraminifera from Rotaliida family in a small grain; (c) calcite crystal (lower right) together with aggregate of elongated barite crystals (in the upper left corner), gypsum crystal (to the right), and irregular pyrite inclusion (in the lower right central part) in a big grain; (d) fragment of diatom frustule in a small grain.

Coffinite is found in the form of oval micrometer-sized crystallites in the colloform phosphatic matrix (Figs. 6c, 7a). Its microdiffraction pattern reveals reflections $d_{011} = 4.67$ and $d_{200} = 3.48$ Å belonging to crystallographic direction [011] of reverse lattice.

Native silver looks like crystalline-like bodies of whimsical form with partly orthogonal edges and a smooth surface, up to several micrometers in size (Fig. 7a). The diffraction spacings of its crystalline lattice are $d_{220} = 1.43$ Å, the crystallographic direction determined by electron beam is [111].

Sternbergite ($\text{AgFe}_2\text{S}_{3-4}$) is found in the form of an elongated micrometer-sized crystalline-like particle inside phosphatized coccolith (Fig. 7b). Diffraction spacings of its crystalline lattice are determined as 4.27, 3.82, and 3.26 Å.

Sellaite (MgF_2) is found in two mounts in the form of a submicrometer-sized oval and irregular particles (Fig. 8a). The microdiffraction pattern of this mineral is monocrystalline. The crystallographic direction determined by electron beam is [112].

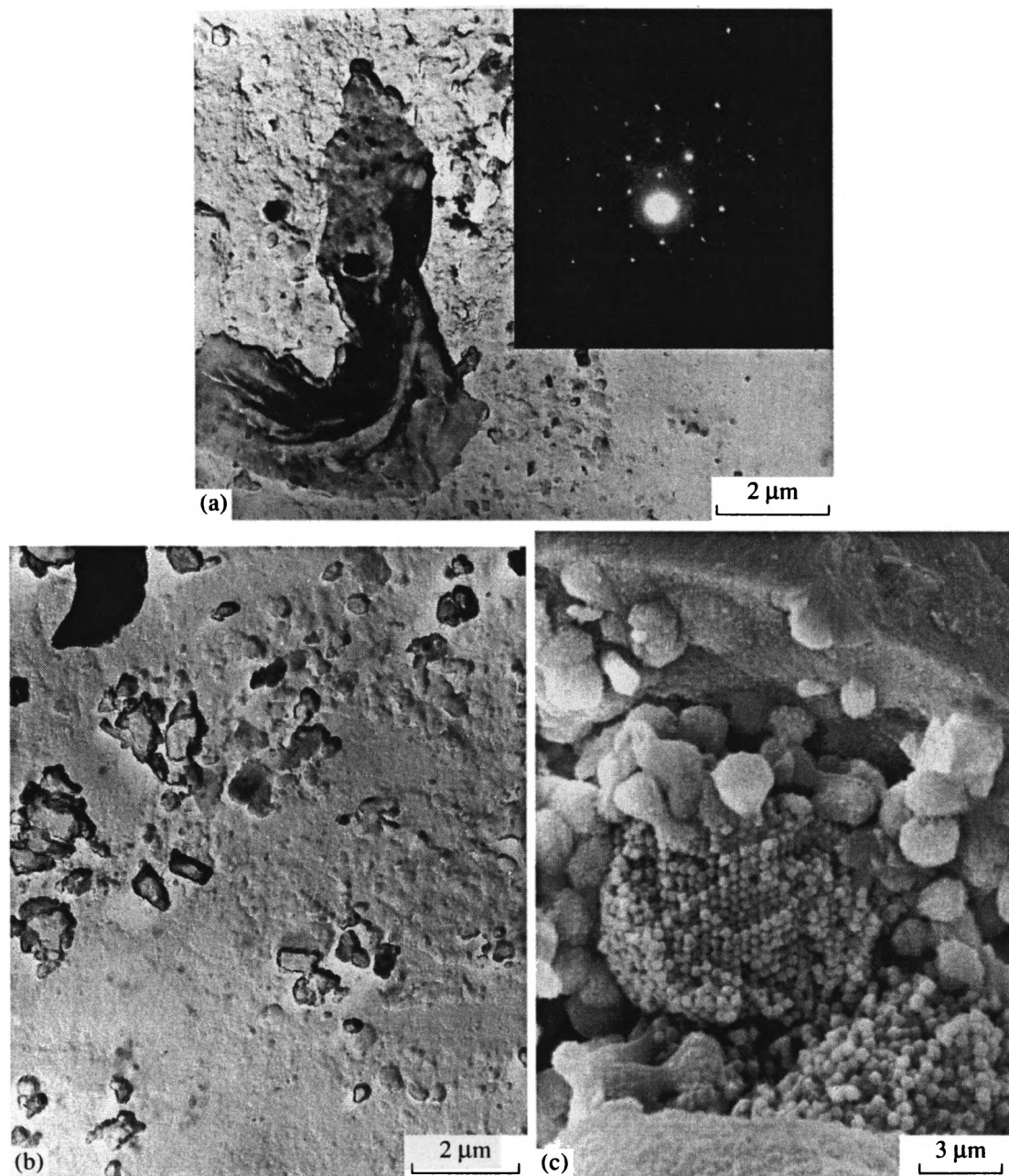


Fig. 4. Illite and pyrite in big grains. (a) Irregular illite particle inside colloform phosphate and microdiffraction pattern of illite; (b) micrometer- and submicrometer-sized pyrite particles disseminated in phosphatic matrix; (c) partially destroyed grains of framboidal pyrite associated with dumbbell-like phosphatic crystallites.

Shercolite $(\text{Ca}_3(\text{Fe}, \text{Ti})_2[(\text{Si}, \text{Ti})\text{O}_4]_3)$ appears as an isometric angular particle of submicrometer size inside the crystalline-like phosphatic matrix (Fig. 8b). Its electron beam determined crystallographic direction is $[112]$ and diffraction spacings are 2.68, 1.67, and 1.25 Å.

RELATION OF MINERAL COMPOSITION OF GRAINS TO THEIR ORIGIN

The rounded nature of grains and the structure of phosphatic deposit present evidence that phosphatic

material was subject to reworking and redeposition during repeated Pliocene–Pleistocene sea level changes. As for mineral composition of phosphatic grains, it is mainly inherited from diagenetic stage of their formation in primary host sediments represented apparently by Pliocene–Pleistocene diatomaceous ooze analogous to recent diatomaceous ooze covering the Namibian shelf to the north of phosphatic sand area. This consideration is supported by the following facts.

The investigation of sediment cores proved the stable character of coastal upwelling regime on Namibian

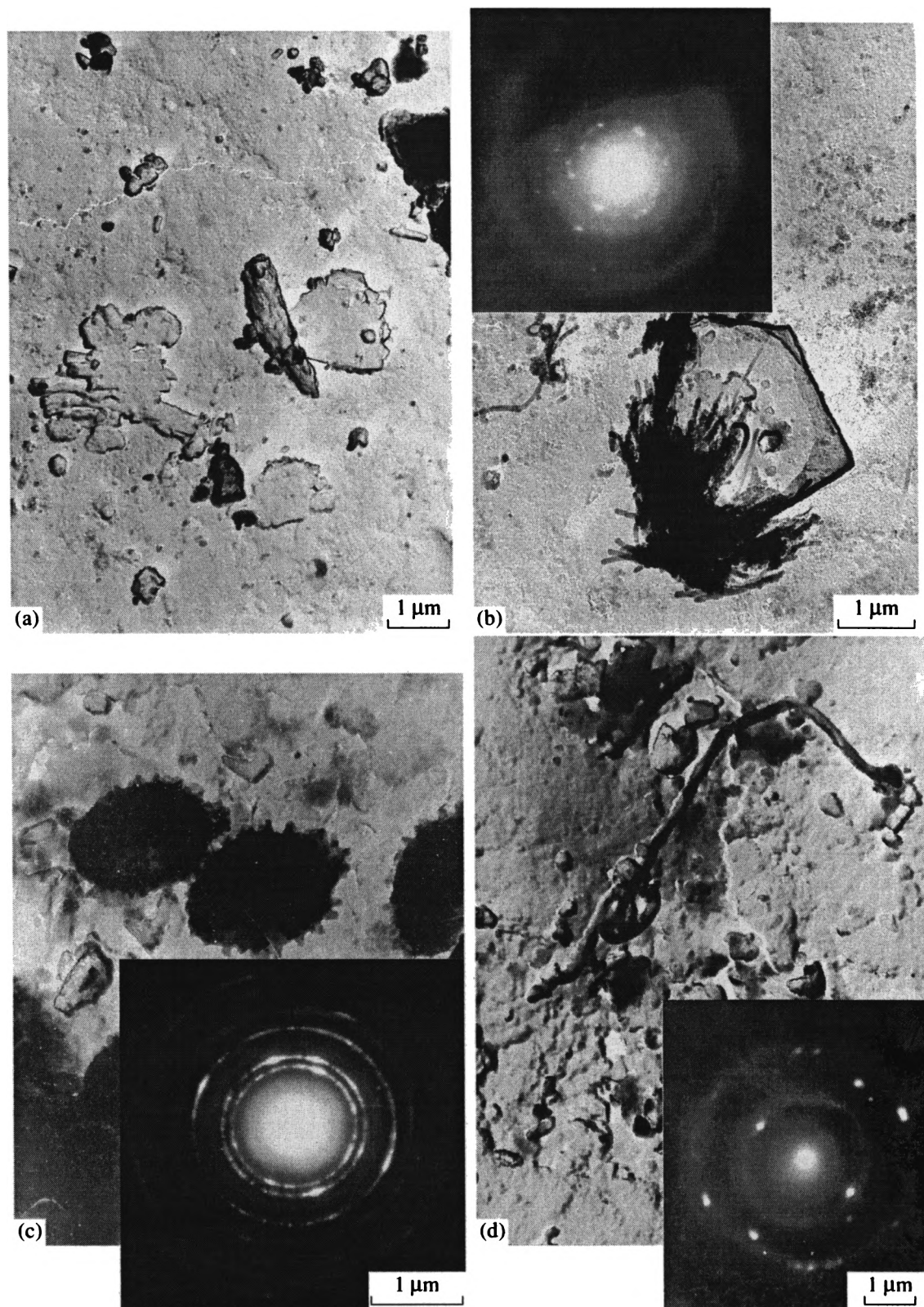


Fig. 5. Barite, illite, and iron minerals in big grains. (a) Irregular barite particle (to the right of the center) associated with two platelets of illite with rugged edges (to the left and above the center); (b) barite crystal associated with aggregate of filamentous ferrihydrite, and barite microdiffraction pattern; (c) bacteria-like particles replaced by ferrihydrite and its microdiffraction pattern; (d) worm-like particle consisting of wüstite and its microdiffraction pattern.

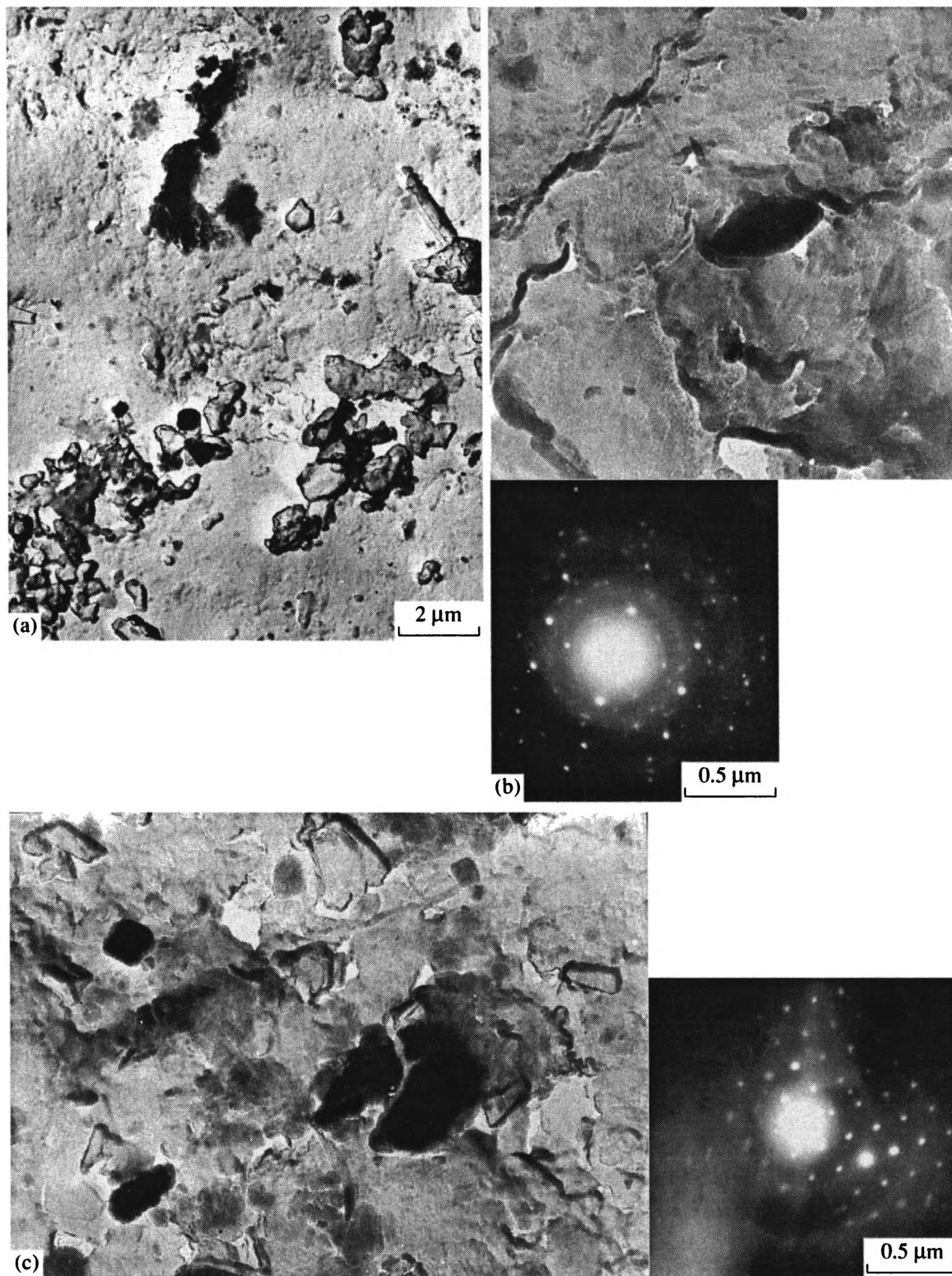


Fig. 6. Monazite and coffinite in big grains. (a) Finely dispersed aggregate and platelets of monazite (upper center), together with aggregate of pyrite grains (in the lower left corner); (b) rhombic crystal of monazite and its microdiffraction pattern; (c) oval coffinite crystal (in the lower left corner) and its microdiffraction pattern, together with pyrite particle (in the upper left corner).

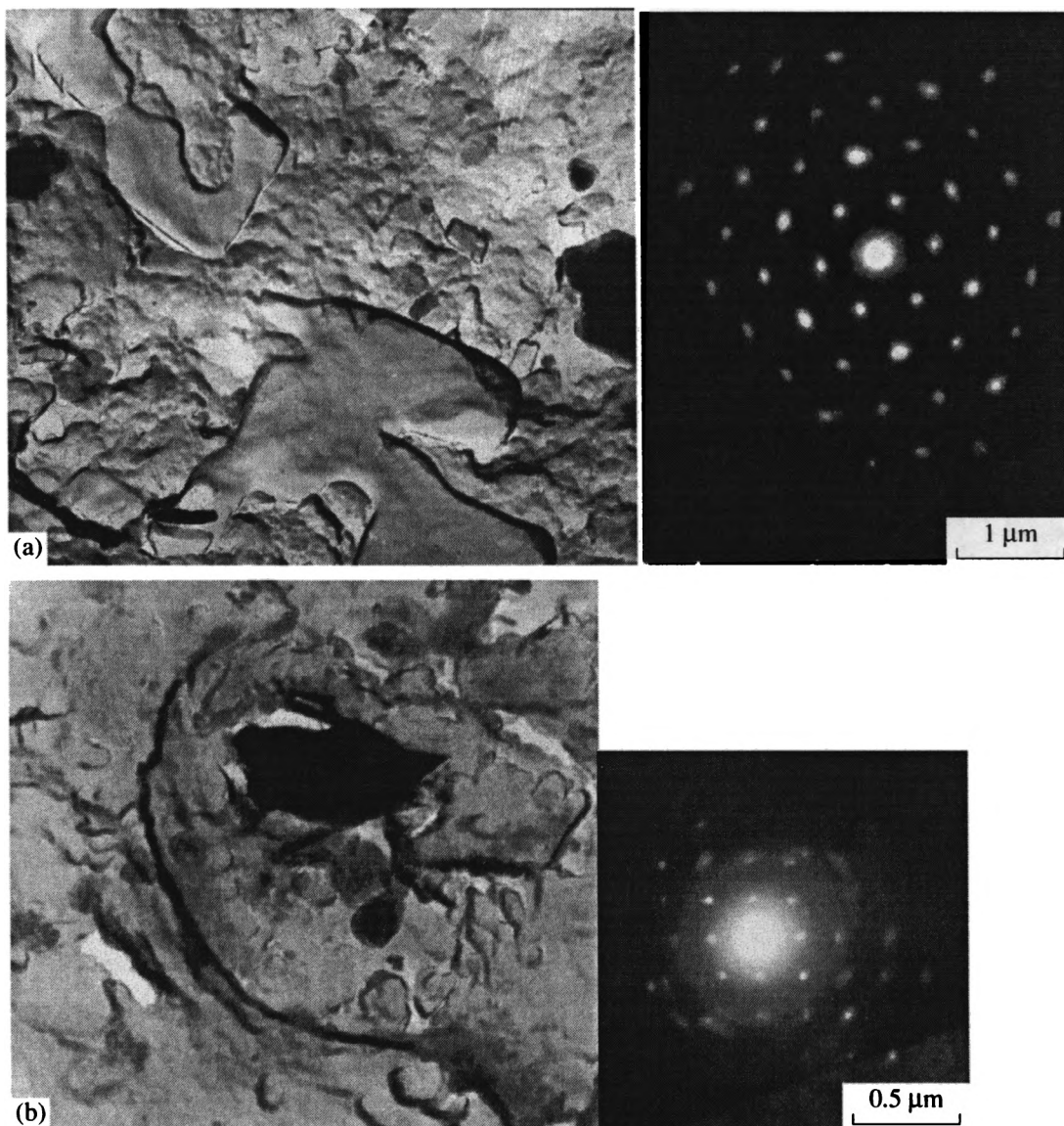


Fig. 7. Native silver and sternbergite in big grains. (a) Irregular smooth-surfaced crystals of native silver (in the upper and lower central part) and its microdiffraction pattern, together with replica-extracted oval coffinite particle (in the upper left corner, to the left of silver crystal), and carbonate particle (near the right edge); (b) elongated sternbergite crystal inside phosphatized coccolith and microdiffraction pattern of sternbergite.

shelf during Pliocene–Pleistocene (Dingle *et al.*, 1996), which supported high biological productivity of phytoplankton and accumulation of biogenic sediments. According to the evidence of diatom remains and molds in phosphatic grains, the latter formed in sediments of such type.

Moreover, the internal structure of these grains is seemingly similar to recent micronodules from diatomaceous ooze described by Baturin and Zhegallo (1997) and Baturin *et al.* (1998a). Both types of grains show similar structure of phosphatic matter, in particular, similar micrometer-sized spindle- and dumbbell-shaped crystallites.

As for nonphosphatic components, the age generations of grains enclose clay minerals (illite), pyrite, barite, and very rare quartz grains, without traces of glauconite. Each of these minerals has a genetic significance.

Illite is considered to be the most characteristic clay mineral common in the near-shore terrigenous mineralogical province of South Eastern Atlantic (Griffin *et al.*, 1968). It is scarce in phosphatic sand, but in recent diatomaceous ooze of Namibian shelf it is common, whereas in a narrow along-shore band stretching between coastal terrigenous sand and diatomaceous

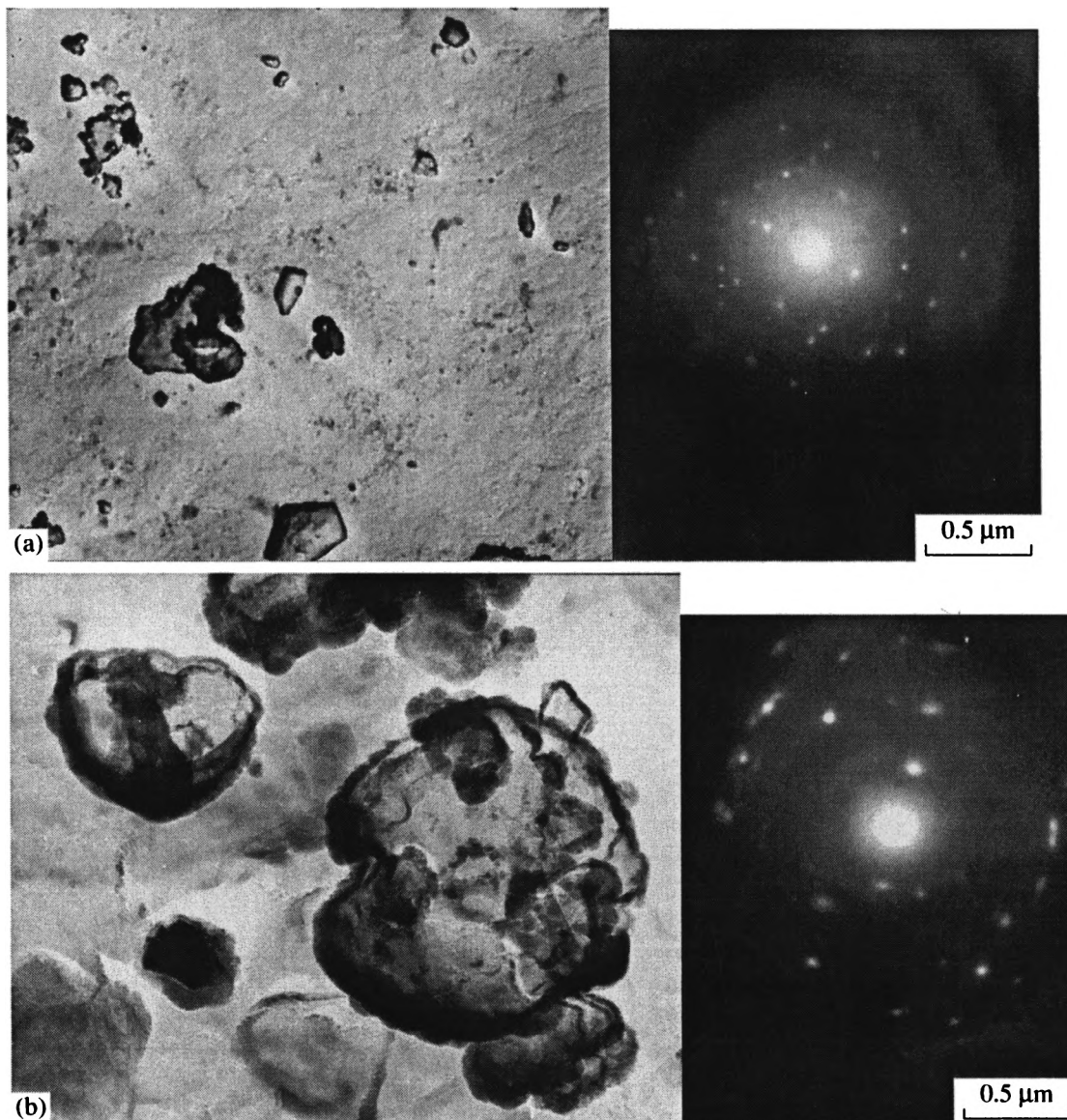


Fig. 8. Cellaite and shercolite in big grains. (a) Irregular cellaite particle (to the left of the center) inside colloform phosphate and microdiffraction pattern of cellaite; (b) rounded particle of shercolite (in the lower left corner) and its microdiffraction pattern; bigger rounded particles are phosphatized coccolith fragments.

ooze its concentration is reaching 40% (Bremner, 1980).

Quartz, on the contrary, is rare in diatomaceous ooze and common in phosphatic sand. Glauconite is absent in diatomaceous ooze and in the studied sample, however, in some places on the outer Namibian shelf, it is found in phosphatic grains as a secondary mineral (Bremner and Rogers, 1990).

It is known that glauconite is related to a suboxic environment and is unable to form in a reducing media characteristic of diatomaceous ooze of the inner Namibian shelf, where Eh values are as low as -200 mV (Baturin, 1978). Direct indicators of a reducing environment are other minerals, especially pyrite that forms

owing to bacterial sulfate reduction in organic-rich sediments as described by many workers (Lein, 1979; Volkov, 1984). According to modern concepts, pyrite is formed during marine diagenesis through one-stage reaction such as $\text{Fe}^{2+} + 2\text{HS}^- + 1/2\text{O}_2 \rightarrow \text{FeS}_2 + \text{H}_2\text{O}$; in this reaction, only Fe^{2+} reduced before initiation of sulfate reduction is taking part, with sulfate provided by marine water (Volkov, 1984). It is possible that wüstite found earlier in marine ferromanganese deposits (Baturin and Dubinchuk, 1984; Fasiska, 1967) represents the relic of such reduced iron.

The first investigators of framboidal pyrite considered these formations as pyritized bacterial colonies, however, analogous framboids were synthesized later

in a laboratory proving their mineral nature (Sweeney and Kaplan, 1973), though bacteria are able to produce pyrite inside their cells (Posfai *et al.*, 1998).

Another mineral that is characteristic of described grains is barite, whose occurrence in sediments is considered by some investigators as an indication of high biological productivity of surface waters (Arrhenius, 1963). Barite in recent diatomaceous ooze on Namibian shelf is actually rather common (Brongersma-Sanders *et al.*, 1980; Price and Calvert, 1978). Well-formed authigenic barite crystals were found in phosphorite nodules forming in these oozes as well (Baturin *et al.*, 1998b).

One more indication of conditions of the formation of phosphorites is the concentration and occurrence form of U in them, since this element is able to accumulate in reducing sedimentary environments (Baturin, 1975; Kolodny, 1981; Kolodny and Kaplan, 1970; Naumov *et al.*, 1963).

Uranium is concentrated in Pliocene–Pleistocene grains (U up to 0.01%) and Recent phosphorite nodules from diatomaceous ooze where U is reduced up to its 4-valency state (Baturin *et al.*, 1974; Veeh *et al.*, 1974).

However, the problem of independent uranium phases in phosphorites remained obscure during a long period. According to classical concepts, U in phosphorites is either incorporated in apatite lattice as an isomorphic substitution for Ca, or remains in a sorbed state (Altschuler *et al.*, 1958; Davidson and Atkin, 1953; Heinrich, 1962; McConnell, 1973; McKelvey *et al.*, 1955).

The presence of independent uranium phases in phosphorites was assumed earlier based on experimental work (Serebryakova and Razumnaya, 1962), but this assumption was distrusted by many people. However, independent uranium phases were found later in phosphatic fish remains from Maikop deposits (Dubinchuk *et al.*, 1978, 1990; Kochenov *et al.*, 1973; Levina *et al.*, 1976), as well as in Holocene phosphorite nodules of the Namibian shelf and in Late Quaternary nodules from the Peru–Chile shelf, where uraninite and ningyosite were determined (Baturin and Dubinchuk, 1978, 1979; Baturin *et al.*, 1986). According to present work, the list of uranium minerals in phosphorites is enlarged owing to coffinite.

The essential geochemical difference of Pleistocene grains from Recent ones is the enrichment of formers and depletion of latters in rare earth elements (REE) as reported earlier (Baturin *et al.*, 1972; Tambiev *et al.*, 1979; Watkins *et al.*, 1995). This phenomenon is interpreted as an indication of secondary nature of REE accumulation which begin to concentrate in phosphatic matter only after it assumes crystalline features. The concentration process depends also on the extent of specific surface of phosphorites and duration of their contact with ambient seawater, as shown by behavior of REE in phosphorites on Pacific seamounts (Baturin and Yushina, 1998).

The studied phosphatic grains have a rather large specific surface and were washed by bottom water of the shelf zone seemingly during the whole Pleistocene which stimulated their enrichment in total REE up to 0.10–0.13% (Baturin, 1999; Watkins *et al.*, 1995). According to most investigators, REE are incorporated in apatite lattice substituting for Ca (Bliskovskii *et al.*, 1969; Kolodny, 1981). However, according to morphology of monazite found in our grains, it is apparently authigenic and was formed due to the concentration of primary colloidal matter, showing the multitude of REE forms in phosphorites.

Native silver and sternbergite were not identified in phosphorites before. Data about Ag enrichment in phosphorites from various regions of the world were presented more than once (Altschuler, 1980; Kholodov, 1973; Kholodov and Bliskovskii, 1976), however, direct information about its occurrence form was absent; it is not yet clear whether described findings of native silver and sternbergite are mineralogical rarities or common form of silver occurrence in phosphorites. Anyhow, sternbergite in some sulfide deposits was known long ago and was described repeatedly (Czarnianske, 1969; Streng, 1878).

It is evident that the problem of U, REE, and Ag occurrence in phosphorites is to some extent similar: all of these elements are able to concentrate in phosphorites 10 to 30 times relative to shale (Altschuler, 1980), but are disseminated either in apatitic lattice or in sorbed state which seems to exclude the possibility to form independent mineral phases.

Nevertheless, such phases exist, at least on a microlevel. It might be related to diagenetic redistribution of these elements in certain microzones of phosphatic matter stimulating their microlevel concentration, exceeding the average concentration many times and leading to formation of independent mineral phases.

The most exotic rare mineral we found is sellaite which was first synthesized in laboratory conditions (Vidal-Valat *et al.*, 1979). According to its chemical composition (MgF_2), sellaite is analogous to fluorite (CaF_2), rather common in metamorphosed phosphorites which lost their carbonic acid along with fluorine in the process of secondary transformations (Krasil'nikova, 1963).

Magnesium, Ca and other cations are able to enter into apatitic lattice (Zanin, 1975). However, phosphorites were not influenced by any metamorphism and contain an appreciable amount of carbonic acid as well as fluorine. Consequently, sellaite could not form according to the scheme suggested for fluorite, and its origin remains obscure.

Among minerals that are not related directly to phosphate accumulation are gypsum, feroxyhyte, and shercolite.

Gypsum is common in some onland phosphorites. For example, its concentration is 0.2% in nodular phos-

phorites of Podobug region, 1.6% in phosphorites of Dniepr–Don and Volga regions, reaches up to 4.5% in some Cambrian Siberian phosphorites, and even >10% in gypsinated Tunisian phosphorites (Smirnov, 1972; Zanin, 1992).

As for oceanic phosphorites, secondary gypsum was found in glauconitized phosphatic pellets outside the diatomaceous ooze area (Bremner, 1980), but it was never found in Recent phosphatic nodules and grains from these ooze.

In oceanic sediments, gypsum was first found in the Southern Atlantic (Bannister and Hey, 1936) and later in other places. Gypsum is often terrigenous in near-shore sediments and authigenic in deep-sea sediments. However, in some organic-rich sediments, gypsum falls out of interstitial water in the course of sediment drying, and represents an artefact (Briskin and Schreiber, 1978; Siesser and Rogers, 1976). In our case, rod-shaped gypsum inclusion is incorporated inside dense phosphatic grain and might be either authigenic or terrigenous, since that single finding does not allow it to have a confident decision.

Feroxyhyte, which was first found in oceanic ferromanganese nodules (Chukhrov *et al.*, 1976), is characteristic exclusively of oxidizing environments and is not related to reducing diagenesis of the initial stage of phosphate accumulation. It was suggested that feroxyhyte forms owing to the oxidation of ferrous iron (Murray, 1979); in our case, it might be a secondary product of pyrite transformation.

Regarding shercolite whose diffraction characteristics are given in reference volume (*Selected...*, 1974), it might be assumed that shercolite is allothigenic and supplied from a terrigenous source.

CONCLUSION

The above data show that redeposited phosphatic grains from Pliocene–Pleistocene sand of the outer Namibian shelf are similar to authigenic phosphatic grains from Recent diatomaceous ooze of the inner Namibian shelf described in (Baturin and Zhegallo, 1997; Baturin *et al.*, 1998a) in structure and mineral composition.

They both consist of phosphatic matter of the colloform, globular, and crystalline modifications. The major biogenic components of both types of grains are fragments of fish bones and scales, calcareous coccolith and foraminifera detritus, and opaline silica of diatoms. Accessory minerals are represented by illite, authigenic pyrite, barite, and rarer inclusions of uranium minerals.

As a whole, these data show that grains described above were formed like their Recent counterparts due to diagenetic redistribution of phosphorus and deposition of calcium phosphate in biogenic sediments whose composition is reflected by inclusions of characteristic biogenic detritus.

One more result of this investigation consists of the identification of a number of minerals that were not previously described in oceanic phosphorites, including coffinite, monazite, native silver, sternbergite, sell-aite, and shercolite. The formation of the first four of these minerals is evidently related to two phenomena: first, enrichment of phosphatic matter in U, REE, and Ag; and second, their diagenetic redistribution and microlevel concentration culminated by formation of independent micrometer-sized mineral phases. Shercolite is probably allothigenic, whereas the origin of cellaite remains unclear.

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Paleogeographic and Geodynamic Environments of Upper Vendian and Cambrian Sedimentary Rock Formation in the Central East European Platform

Yu. E. Dmitrovskaya[†]* and T. N. Kheraskova**

* The NEDRA State Scientific Industrial Enterprise, ul. Svobody 8/38, Yaroslavl, 150000 Russia

** Geological Institute (GIN), Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 109017 Russia

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Abstract—On the basis of the complex study of Upper Vendian and Cambrian sedimentary rocks, the structural and facies schemes of central East European Platform were compiled for the Rovnian (Nekrasovo), Middle Cambrian (Urdoma), Middle–Late Cambrian (Tolbukhino), and Late Cambrian (Nikolsk) times. It has been shown that the internal structure, the basin topography, and the facies distribution in the Moscow marine basin of the Russian Plate were controlled by relative displacements of large basement blocks and by motions along faults, which bounded the Riphean aulacogens, and along the Polotsk and Rybinsk transverse faults. The strait-shape character of basins was inherited from the Riphean rift structure. The marine transgressions of that time streamed out from the western districts of platform. The intensity and timing of transgressions were to a great extent controlled by structural transformations in Caledonian paleoceans.

INTRODUCTION

Vendian and Cambrian sedimentary rocks at the East European Platform were penetrated by deep boreholes in the early 1950s. Over the years, the considerable body of works concerning the stratigraphy, sequence of deposition, and present-day occurrence was carried out (Burzin, 1996, 1998; Dmitrovskaya, 1988, 1993; Dmitrovskaya and Kheraskova, 1997; Dmitrovskaya *et al.*, 1983, 1995; *Fatsii i stratigrafiya...*, 1991; Garetskii, 1997; Gorbatshev and Bogdanova, 1993; Igolkina *et al.*, 1981; *Istoriya razvitiya...*, 1981; Kirsanov, 1970; Kir'yanov, 1975; Mens, 1980; Mens and Pirrus, 1986; Olovyanishnikov, 1998; Rozanov, 1980; Sokolov, 1997; *Stratigraficheskaya skhema...*, 1996; Sturt and Robberts, 1978; *Tektonika...*, 1991; Valeev, 1978; Volkova and Kir'yanov, 1995). The resumption of petroleum exploration in the Moscow Syncline stimulated the further study of paleogeographic, sedimentological, and paleotectonic environments of sedimentation in this region.

The present-day field of Upper Vendian (Rovnian) and Cambrian rocks in the sedimentary cover of the East European Platform is confined to the zone of the large lineament, which separates the structures of the Fennoscandinavian and the Volga–Urals basement blocks. According to (Garetskii, 1997; Gorbatshev and Bogdanova, 1993), the Volga–Urals block is mainly composed of Archean crust while the Fennoscandinavian block is subdivided into two segments: Archean Belomorian–Karelian and mainly Early Proterozoic Baltic–Belorussian (Fig. 1). The aim of this

work is to establish how the relative displacements of large blocks and motions along less significant faults in cratonic basement affect the distribution of Upper Vendian–Cambrian sedimentary rocks, their facies, and degree of preservation of sediments deposited in the epicontinental basin. Another problem is related to the elucidation of causes, which gave rise to the structural rearrangement of the epicontinental basin at the Early–Middle Cambrian boundary and middle Late Cambrian.

The main attention was attracted to four rock complexes: Nekrasovo, Urdoma, Tolbukhino, and Nikolsk (Dmitrovskaya *et al.*, 1995; *Stratigraficheskaya skhema...*, 1996), which characterize principal evolution stages of the central East European Craton in Late Vendian and Cambrian. The reconstruction of sedimentation environments and the paleogeography of the Late Vendian and Cambrian basins, as well as recovery of paleostructures, which affected the sedimentation of that time, is hindered by an incomplete preservation of sediments of that age and their partial erosion during the subsequent structural rearrangements, migration and inversion of some structures through time. However, the paleoreconstruction on the basis of complex basinal analysis is necessary for a coherent understanding of the evolution of the lower sedimentary cover of the East European Craton.

ROVNIAN (NEKRASOVO) TIME

The Rovnian Horizon was deposited during the Nekrasovo time. This horizon is correlated with the Nekrasovo Formation in the Moscow Syncline and

[†] Deceased.

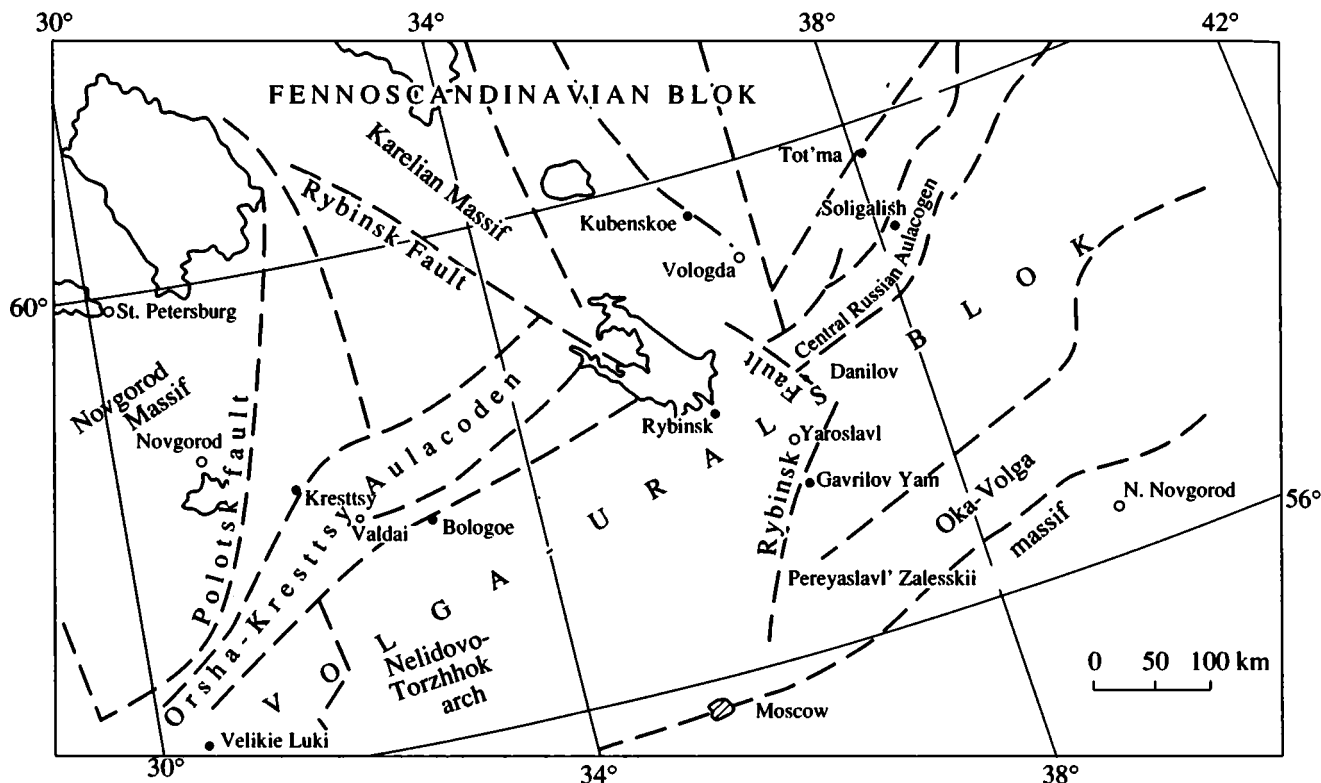


Fig. 1. Faults in basement of the central East European Platform, after Valeev (1978).

with the Lomonosovo Formation in western districts (Rozanov, 1980; Sokolov, 1997; *Stratigraficheskaya skhema...*, 1996). These rocks are conventionally referred to Upper Vendian. Recently, the Rovnian rocks are suggested to be the lowermost unit of Cambrian (Sokolov, 1997; *Stratigraficheskaya skhema...*, 1996).

The rock complex under consideration is represented by red and variegated terrigenous marine deposits, which unconformably (with an erosion at the base) overlie various units of the Reshma Formation (Kotlian Horizon of Upper Vendian). Three facies related to specific paleogeographic and geodynamic environments are recognized: (1) gray sandy rocks, <20 m thick, (2) variegated and red sandy rocks, 30–120 m thick, and (3) silty-clayey rocks, 20–33 m thick (Fig. 2).

The facies of gray sandy rocks occurs in the northwest (Stolbovo, Siversk, Tosno, and Khaalovo boreholes) and south (Kuvshinov, Maksatikha, and Pereyasavl' boreholes) of the region. The area of this facies is related to zones, which are located on the periphery of inferred areas of erosion and removal of sedimentary material from the Baltic segment of the Fennoscandian block and the Nelidovo-Torzhok arch, a fragment of the Volga-Urals block (Figs. 1, 2). The erosion of underlying rocks (Kotlian Horizon) increases toward the area of this facies, which is characterized by a restricted thickness and greenish gray color. The layer of inequigranular quartz-feldspar sandstone with an

admixture of gravel consisting of phosphatized rocks commonly occurs at the base. This rock testifies to the relatively fast sea invasion. Upward, the sandstones become more homogeneous with a predominance of quartz grains. The glauconite admixture appears. Interlayers and lenses of siltstone and clay, commonly of hydromicaceous composition occur among sandstones, especially in the middle part of section. In the north, the hydromica in the clayey fraction is complemented by the kaolinite, which presumably indicates the erosion of weathered rocks of the Fennoscandian block. Chlorite, mixed-layered clay minerals, and degraded biotite were detected to the south as products of rewashing of underlying Vendian rocks (Igolkina *et al.*, 1981; *Istoriya razvitiya...*, 1981). The flat wavy and horizontal bedding is typical. In environs of St. Petersburg, the remains of worms (*Serpulites*) were found in the sandstone.

Structures of sedimentary rocks allow to suggest their deposition in the onshore zone of shallow-water epicontinental sea during the transgression.

The facies of variegated and red sandstones and siltstones are widespread in the southeastern and northeastern parts of the basin (Fig. 2). The large thickness is a typical feature. The increase in thickness toward the Oka-Volga massif (a fragment of the Volga-Urals block) and the eastern Fennoscandian block indi-

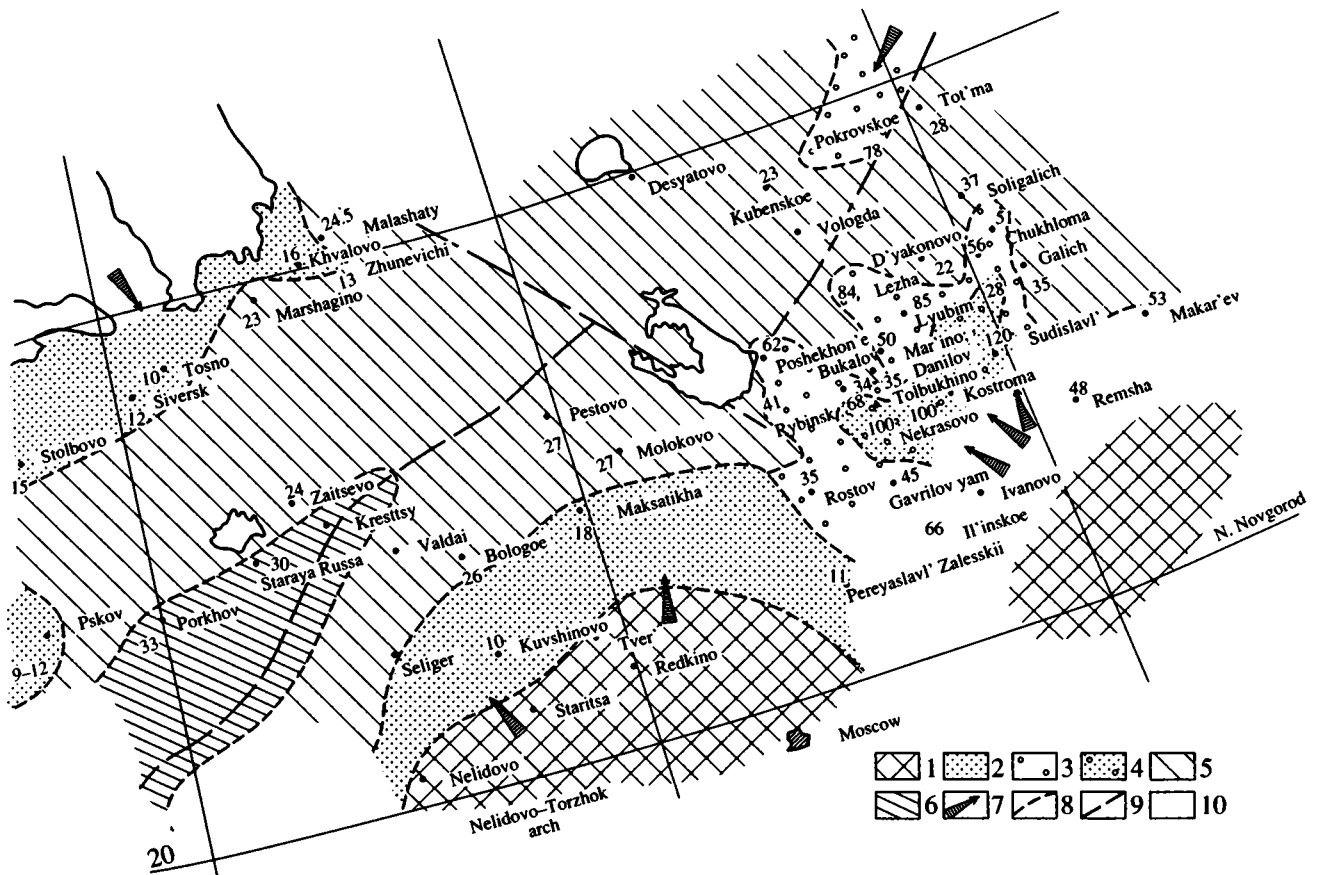


Fig. 2. Structural and facies scheme of the central East European Platform for the Nekrasovo (Rovno) time, Late Vendian. (1) Inferred areas of erosion; facies: (2) gray sandstones, (3) variegated mainly sandy rocks, 30–80 m thick, (4) variegated mainly sandy rocks, > 80 m thick, (5) mainly gray silty-clayey rocks, 20–30 m thick, (6) mainly gray silty-clayey rocks, > 30 m thick; (7) direction of clastic material removal; (8) facies boundary; (9) faults in basement suggested to be active in the time under consideration; (10) thickness, m.

cates the existence of local provenances, which supplied the voluminous clastic material.

The facies are characterized by a diversity of rock compositions and colors. Intercalated sandstones, siltstones, and argillites are predominant. The sandstones represent fine- to coarse-grained quartz-feldspar and quartz (often glauconite-bearing) rocks with light gray, greenish gray, and reddish brown colors. The coarse-grained sandstone is distinguished by poor sorting; quartz pebbles and gravel are occasionally encountered. Zircon, tourmaline, and anatase were reported among accessory minerals (Kirsanov, 1970). Sandstones to some or other degree enriched in clay material are most abundant. However, the light gray and greenish gray inequigranular sandstones do not contain a clay admixture. They resemble the skeletal sand, which underwent repeated rewashing and redeposition. Siliceous and ferruginous cement is typical of such sandstones. The siltstones are light gray, light green, and reddish brown, compact, mainly quartz-micaceous; they contain a clay admixture. The gray-colored varieties contain glauconite. The argillites are mainly hydro-

micaceous, light green, dark gray, and reddish brown; they are often enriched in silty material or contain thin siltstone interlayers. Worm trails and small thin sabeliditides (Rostov and Danilov boreholes), and mat-forming cyanobacteria are abundant in argillites (Burzin, 1998).

The horizontal, lenticular, cross-wavy, crisscross-wavy bedding, and current lamination are observed. The slumping structure (Lyubim borehole) allows to infer a somewhat rugged floor of the basin. In addition, the interlayers of homogeneous sandstone, 2–3 m thick, with a clear erosional contact at the base were encountered in the Gavrilov Yam borehole. In terms of structure, they are similar to deposits of grain flows and also indicate some slope of the floor. The grain size of sandstones decreases and the amount of silty and clayey rocks increases upward the section and inward the basin. Likely, this is caused by a sequential widening of the basin during the Nekrasovo time.

It may be suggested that the facies of variegated sandstones and siltstones make up two clinoforms in the northeast and southeast of the basin. The thickness

of the clinoforms is reduced toward the center of basin. Thus, the clinoforms mark the subsidence zones that are completely (Tolbukhino, Nekrasovo, Sudislavl', and Bui boreholes) or almost completely (Pokrovskoe, Poshekhon'e, Lezha, Orekhov, and Chukhloma boreholes) compensated with sediments. Most likely, the sediments of submarine deltas and fans were predominant. This interpretation is consistent with the variation in rock composition, their structures and abundance of red-colored rocks. Marine sedimentation was the dominant type. The continental sediments of lacustrine-lagoonal type were deposited only during short time spans at local sites, especially in the lower part of the section, e.g., in the Nekrasovo borehole.

The facies with a prevailing of silty and clayey sediments are developed most extensively and confined to the central part of the basin where they spatially coincide with the Central Russian Aulacogen. The thickness of rocks related to these facies slightly increases to the southwest, likely due to the general deepening of the sea toward the Volyn-Orsha Basin.

The greenish gray and dark gray silty argillites and argillites proper are most abundant. The red-colored rocks appear in the zone transitional to the facies of variegated sandstones and siltstones (Molokovo, D'yakonovo, and Tot'ma boreholes). In addition, the argillites and silty argillites contain thin (1 mm–1 cm) siltstone interlayers and lenses. Sporadic interlayers of homogeneous fine-grained sandstone, 5–20 cm thick, occur mainly in the lower and upper parts of the section. Siltstones and sandstones are mainly composed of quartz; some of them are enriched in glauconite. The rocks are carbonate-free. Only in the extreme southwest, i.e., in relatively deep-water zone transitional to the Volyn-Orsha Basin (Toropets borehole), the dolomitic-clayey cement was reported in sandstone (data of L. Pachkyavichens cited by Nikishin *et al.*, 1996). This is additional evidence in favor of the general plunge of the basin floor to the southwest.

Dark-gray films of organic matter and abundant tracks of wormlike organisms, as well as trails of mud-eaters ("trace fossil" assemblage) are seen at bedding surfaces of argillites.

Argillites and siltstones are homogeneous or reveal a microlayered lamination, which is typical of current-related sediments. Thin interlayers and lenses of siltstone most likely indicate the microchannels and furrows made by near-bottom currents. Interlayers of uniform, clay-poor sandstone have the structures typical of grain flow sediments.

Structures of slumping and flow of nonconsolidated sediment are occasionally observed in argillites and siltstones (Molokovo borehole) indicating a somewhat rugged topography of the basin floor, probably in proximity to faults in basement, which bound the Central Russian Aulacogen.

The analysis of rock composition, facies and thickness distribution of sediments related to Nekrasovo

(Rovnian) time draws some conclusions concerning the paleogeography and paleostructure of the epicontinental basin, which existed at the Vendian-Cambrian boundary in the central East European Platform. The sediments of that time indicate the onset of great transgression, which reached its maximum at the beginning of Early Cambrian (see below).

The terrigenous sedimentation dominated in the basin of Nekrasovo (Rovnian) time. The green-colored sandstones and siltstones prevailed in onshore zones. The thickest variegated sequences were deposited under conditions of submarine delta. Relatively thin and deep-water silty-clayey sediments were predominant in central part of the basin.

The basin was strait-shaped and located above the Orsha-Kresttsy Aulacogen (Rift). It was subsided toward the larger Volyn-Orsha (Volyn-Podol, according to other authors) Basin (Garetskii, 1997; Nikishin *et al.*, 1996), which connected the basin under consideration with the Yapetus paleocean (Bessonova *et al.*, 1980; *Tektonika...*, 1991).

The existence of tectonic escarpment along the Tot'ma Fault with the subsided northwestern wall is deduced from the sharp difference in thickness of Nekrasovo sediments on opposite sides of this fault (Figs. 1, 2). The thickness of the Nekrasovo Formation is 28 m at the southeastern wall (Tot'ma borehole) and increases up to 78 m at the northwestern wall, 50 km to the west (Pokrovskoe borehole).

The extensive development of "trace fossils" assemblage indicates the shallow-water environment in the central part of the basin (Rozanov, 1980). If the adjacent facies of variegated sandstones and siltstones, up to 120 m thick, are assumed to be deposited in a subsidence zone completely compensated by the extremely shallow-water sediments and the silty-clayey facies was formed in environment of noncompensated subsidence, then the greatest depth of the basin in Rovnian time hardly exceeded 100 m.

According to Rozanov (1980) and Burzin (1998), the fauna and flora in the basin was not too diverse. The phytoplankton and mat-forming cyanobacteria undoubtedly were abundant. Most likely, the fauna was suppressed owing to the mass supply of fresh water from the northeast and southeast, where the submarine delta facies were outlined.

THE LEZHA AND GALICH TIME (EARLY CAMBRIAN)

Lower Cambrian (Tommotian Stage) sedimentary rocks are poorly preserved in the central East European Craton due to the weathering and intense erosion during the regression and great structural rearrangement of this territory in the late Early Cambrian. Most likely, the structural transformation was a response on the collision and thrusting of nappes over the margin of East European Craton at the Timan (Olovyanishnikov,

1998) and the northern Norway (Sturt and Roberts, 1978). Because of this, we shall restrict our consideration to the general description of rocks of this age (Lezha and Galich formations) and environments of their deposition.

The Earliest Cambrian in the central East European continent was characterized by a further development of the marine transgression that started in Rovnian time. Silty-clayey sediments, up to 170 m thick, dominated over all of this territory. They conformably, with a gradual transition, overlay sandy sediments of the Nekrasovo Formation. Dark gray and greenish gray argillite-like clay and argillite of hydromicaceous composition occur in the lower part of the section. The homogeneous structure and separate thin interlayers of quartz siltstone and fine-grained mostly quartz sandstone are characteristic. The sandstone locally contains an insignificant admixture of feldspar and is substantially enriched in glauconite. Upward, the bluish gray argillite-like clay and argillite close in composition to the above rocks are predominant. However, they are distinguished by the microlayered lamination, accumulations of silty material at the layer surfaces, and thin interlayers of quartz siltstone, which also have the microlayered texture.

In the east of the territory (to the east of the Vologda meridian), the clayey microlayered rocks are still more extensively developed. The ubiquitous ripple marks indicate the substantial role of currents in deposition and redeposition of the sediments. In addition, the redstones occur here.

In the upper part of the section (Galich Formation), the relatively coarse-grained rocks appear again as interlayers and lenses of quartz siltstone and glauconite-bearing quartz-feldspar sandstone. This is likely a consequence of the thrusting at the Timan and the related increase in supply of clastic materials from the northeast.

The rocks of the Lezha and Galich formations described above probably characterize only a central part of the Early Cambrian basin. The coastal and onshore facies were not preserved. According to Igolkina *et al.* (1981), the contribution of sandy material to Lower Cambrian clayey sediments increases toward the Belorussian massif in Estonia and in the extreme northeast near the Timan Range. The appearance of relatively distal facies above the proximal facies of the Rovnian time indicates that the Tommotian basin was wider than the Rovnian one and spread far beyond the contour of the present-day occurrence of Lower Cambrian rocks. According to data reported by Igolkina, the Early Cambrian basin surrounded the Baltic Shield as a wide arc, reached the northern Timan in the northeast and approached the Estonia and Volyn-Podol region in the west and southwest. Undoubtedly, it was connected with the Yapetus paleocean in the west and with the Asian paleocean on the Uralian side. At that time, the latter ocean was characterized by an

intensive opening and the formation of new oceanic crust.

The organic world of the Tommotian basin was more diverse in comparison with that of Rovnian time. In addition to acritarchs, fragments of sabellidite and platysolenite tubes, the remains of Vendotenia, Tyrasotenia, and Dvinia have been found. The bioturbation by fossorial organisms was intensively developed. Judging from widespread "trace fossils" facies, the shallow-water environment of Early Cambrian basin in the central East European Craton and fairly complete compensation of subsidence by a sedimentation may be assumed.

THE URDOMA TIME (MIDDLE CAMBRIAN)

The Middle Cambrian is represented by the Urdoma and lower Sablino formations (Dmitrovskaya *et al.*, 1995), which entirely cover the central and western parts of the East European Platform. They unconformably (with an erosion) overlie the Lower Cambrian rocks and mark the onset of the new stage of evolution of the East European Craton, which began after the uplift and erosion in the end of Early Cambrian.

The Urdoma complex is represented by fine- to coarse-grained sandstones with a gravel admixture and gritstone interlayers. Siltstone and clayey siltstone interlayers locally occur, mainly in middle and upper parts of the section. The light gray and greenish gray colors are predominant. Separate units of pink and dark brown terrigenous rocks were encountered in the east.

The Urdoma rock complex comprises three sandstone facies: (1) < 10 m thick, (2) 10–30 m thick, and (3) > 30 m thick (Fig. 3).

The sandstone facies, < 10 m thick, spread over the northwest of the territory (Mel'nitsa, Krasnye Gory, Siversk, Marshagino, Kuti, and other boreholes) and occur in the west, where it covers a small area near the Porkhov borehole. The facies are represented by the white and light gray well-sorted fine-grained quartz sandstone with horizontal and cross bedding. The good sorting, monomictic composition, the absence of a clay admixture, the structure typical of shallow-water sediments refer these rocks to sediments of submarine shoals, barrier beaches, and bars, where they were formed under conditions of repeated rewashing and redeposition giving rise to the formation of so-called skeletal sand. These facies likely characterize the apical part of submarine uplift. It may be suggested that the Novgorod massif—a fragment of the Baltic-Belorussian segment of the Fennoscandian basement block—began to rise up at that time. Subsequently, in the Late Cambrian and Ordovician, this massif separated the basins of the Baltic and Moscow synclises (Dmitrovskaya and Kheraskova, 1997).

The sandstone facies, 10–30 m thick (Fig. 3), mostly comprise of fine-grained and clay-rich Middle Cambrian rocks. This is a light-colored, well-sorted fine-

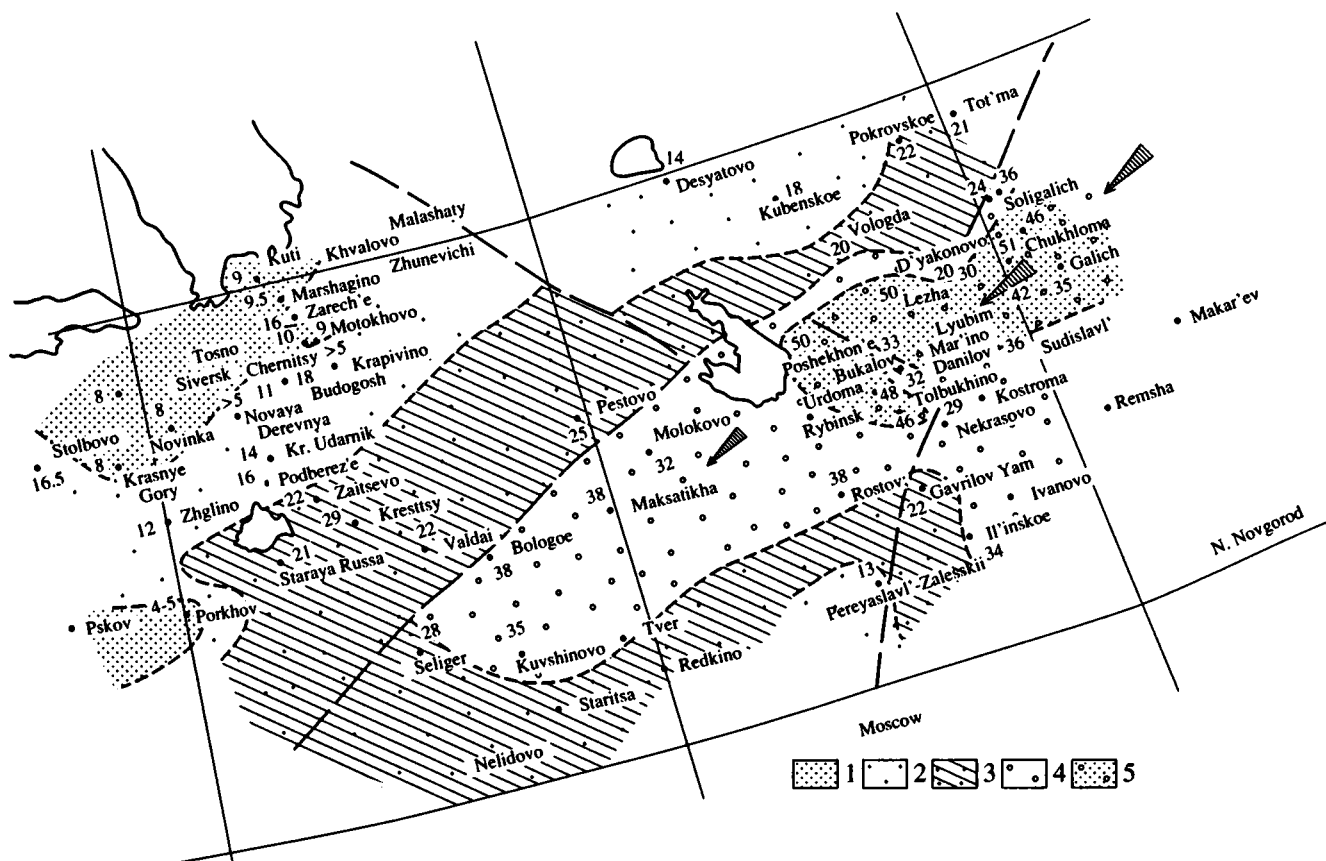


Fig. 3. Structural and facies scheme of the central East European Platform for the Urdoma time, Middle Cambrian. Sandstone facies and thickness: (1) sandstone only, < 10 m, (2) with siltstone interlayers, 10–20 m, (3) the same, 20–30 m; (4) with gritstone and siltstone interlayers, 30–40 m, (5) the same, > 50 m.

grained quartz sandstone with separate thin (< 10 cm) interlayers of gray and dark green, occasionally light gray (in the west) clay, silty clay, and siltstone. The clayey rocks reveal a thin horizontal current lamination. Mud-eater trails are rarely seen on the layer surface (Kubenskoe borehole). In the western part of the territory, the amount of clay increases down the section. It is likely caused by an erosion of underlying Lower Cambrian clayey rocks and their weathering products. Most likely, these facies characterize the most distal and deepest parts of Middle Cambrian basin (Fig. 3).

The sandstone facies, 30–50 m thick, extend as a wide apron along southern walls of the Soligalich and Bologoe faults, which in former times bounded the Central Russian and Orsha–Kresttsy aulacogens. The thickness of these facies smoothly decreases from the northeast to southwest. This suggests that most of the clastic materials was supplied from the northeast, i.e., from eroded tectonic nappes of the Timan.

The facies are represented by gray and light gray, occasionally yellowish and pink quartz sandstones. Fine- to medium-grained and inequigranular sandstones with a gravel admixture are predominant. Commonly, they are poorly sorted and contain a clay admix-

ture; the wavy and cross bedding is typical. The sandstones likely made up the submarine channels of the fore-delta, through which the clastic material was supplied into the Middle Cambrian basin of the East European Craton.

The fine-grained massive variety consisting of well-sorted rounded quartz grains is recognized among the sandstones. It resembles the skeletal sand, which prevails in the above sandstone facies of small thickness. This variety was most likely formed at submarine shoals and bars within a tidal zone, where the clastic material was repeatedly agitated and redeposited.

The sandstones contain interlayers, lenses, and isolated members of siltstone and clayey siltstone of greenish gray, gray, less frequently, brown and violet colors. Charred algae remains were found. The thin horizontal and microwavy current lamination is typical of the siltstones. They contain mud-eater trails and remains of inarticulate brachiopods. These sediments were likely deposited under conditions of low-mobile water.

Thus, the Middle Cambrian basin in the central East European Craton arose due to the transgression, which spread from the west and southwest. The intense supply

of clastic material from the northeast provided the sand deposition. The general slope of the basin was directed to the southwest. In the Late Vendian and Early Cambrian, the basin opened toward the Volyn–Orsha Basin in the marginal part of the Yapetus paleocean.

The basin in the central East European Craton was shallow-water and favorable for the rewashing and redeposition of sediments. As compared with the Early Cambrian basin, the area of the most intense subsidence was shifted southward beyond the limits of Central Russian Aulacogen. It was likely related to the uplift of the Fennoscandinavian block, especially to the uplift of the Novgorod massif, which subsequently separated the basins of Moscow and Baltic synclises (Dmitrovskaya and Kheraskova, 1997).

It may be inferred that in the Urdoma time, the displacements along the Bologoe and Soligalich faults took place; in Riphean, they bounded the southern wall of the Central Russian Aulacogen. On opposite sides of these faults, the thickness of the Middle Cambrian sequence is markedly changed due to the different degree of subsidence compensation by sediments (Fig. 2). The south-faced tectonic escarpments along the Soligalich and Bologoe faults prevented the supply and spreading of clastic material toward the north and northwest.

The shallow-water environment, the abundant supply of clastic material, the rather active hydrodynamic regime, and probably the freshening of water inhibited the evolution of organic life. The fossils are rare and mainly represented by valves of inarticulate brachiopods and remains of microphytoplankton (acritarchs).

THE TOLBUKHINO TIME (MIDDLE–LATE (?) CAMBRIAN)

The sediments of the Tolbukhino time comprise the Tolbukhino and upper Sablino formations (Dmitrovskaya, 1988; Dmitrovskaya *et al.*, 1995; Garetskii, 1997). They conformably (with a gradual transition) overlie the Urdoma sandstones. The sedimentary rocks of that time are preserved only locally due to their partial erosion during the great structural rearrangement and the new sea transgression in Late Cambrian. This causes problems in the study of Middle–Upper Cambrian rocks.

The Tolbukhino rock complex is represented by an intercalation of dark gray and gray argillites, siltstones, and less frequent sandstones with remains of inarticulate brachiopods, trilobites, and acritarchs. The thickness varies from a few meters to 50 m. The Tolbukhino rock complex comprises three facies (1) the facies of sandstones having a small thickness, (2) the sandy–silty facies, 10–30 m thick, and (3) the silty–clayey facies, 30–50 m thick (Fig. 4).

The sandstone facies of a small thickness is similar to the same facies of skeletal sand in the underlying Urdoma complex. Commonly, both are united into the

Sablino Formation. As before (in the Urdoma time), the thin sandstone units are related to submarine shoals and bars at the tops of flat uplifts and were formed at the crest of growing Novgorod uplift (Fig. 2). However, in the Tolbukhino time, the sandstone was also deposited in the north of basin (Desyatovo and Vologda) indicating the initial uplift of the Karelian segment of the Fennoscandinavian block of basement.

The facies of silty–clayey rocks, 30–50 m thick, occurs as a zone extended in the northeastern direction in the central part of the Tolbukhino time basin. This zone partly inherits the most subsided area of the preceding Urdoma time and the grabens of the Central Russian and Orsha–Kresttsy aulacogens. Two local basins most compensated by sediments are outlined within a field of these facies (Fig. 4).

Siltstone and argillite are the most abundant rocks. They contain subordinate interlayers and small lenses of fine-grained quartz sandstone, to some or other degree enriched in clay material. The fine, not rounded, detritus of inarticulate brachiopods is occasionally contained in sandstone; traces of slight erosion of underlying sediment are noticed.

The gray and dark gray greenish clayey siltstone reveals horizontal lamination, and less frequently, wavy-layered flow bedding. It also contains poorly preserved and displaced remains of inarticulate brachiopods and trilobites and their detritus. The fine outwashed shell detritus is confined to layer surfaces and indicate a rather high velocity of currents.

The argillites are represented by greenish gray, commonly silty varieties. Similar to the siltstones, they reveal a current lamination and bear the marks of symmetric and asymmetric fine wavy ripples. In some boreholes, e.g., in the Molokovo borehole, the primary structure of sediments is disturbed by bioturbations. Primary clots of inarticulate brachiopods have also been found here. These areas likely characterize the quiet conditions in local sinks of the bottom relief. However, much more frequently, the sediments bear indications of deposition in mobile water (current-related sediments are predominant).

The facies of sandy–silty rocks, 10–30 m thick, occupies a transitional position in the basin of Tolbukhino time. Most likely, this facies is related to slopes of the strait-shaped basin. The facies is also of transitional character. In comparison with the facies of most subsided part of the basin and the greatest thickness of the Tolbukhino Formation, the number of sandstone interlayers increases, and the clayey rocks virtually disappear. This indicates that the sediments were periodically agitated at uplift slopes; the clay fraction was washed out and removed to the deep parts of the basin.

The basin of Tolbukhino time was strait-shaped with a rather strong longitudinal current. Sandstones and siltstones likely mark separate microchannels of those currents, sites of their discharge or change of velocity.

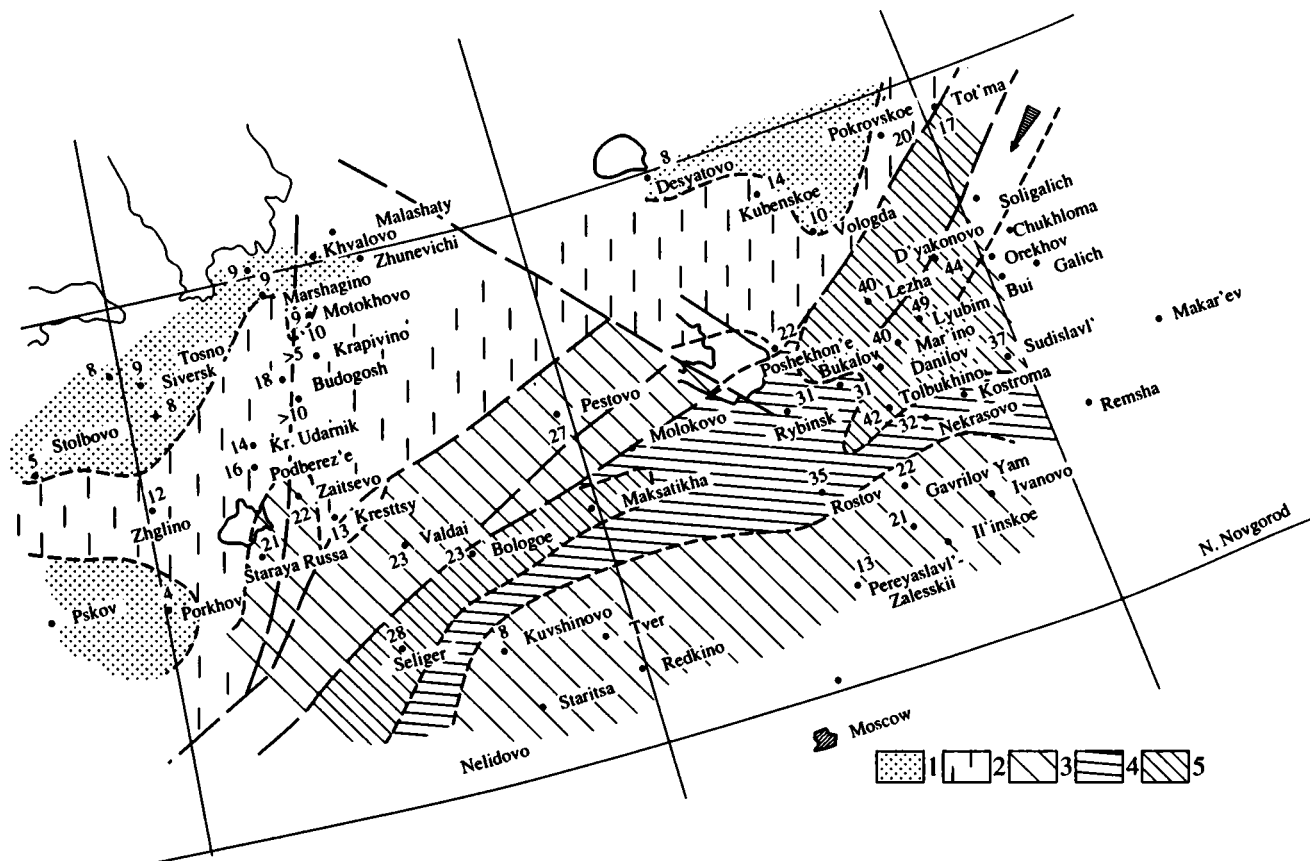


Fig. 4. Structural and facies scheme of the central East European Platform for the Tolbukhino time, Middle-Late Cambrian. *Facies:* (1) sandstones, thickness < 10 m, (2) sandstones and siltstones, 10–20 m, (3) the same, 20–30 m, (4) silty and clayey rocks, 30–39 m, (5) the same, ≥ 40 m thick.

Two local basins with the greatest thickness of the Tolbukhino structural and facies complex are outlined within a field of silty-clayey sediments; the basins are separated by a small saddle of the northwestern direction (Fig. 4). The saddle was related to strike-slip displacements along the Rybinsk Fault, which subsequently divided the formerly single Orsha–Central Russian Aulacogen cut by transverse faults into two grabens: the Orsha–Kresttsy and the Central Russian proper.

As in Nekrasovo and Urdoma times, the reactivated faults of Tolbukhino time inherited rifting from the Riphean. The Tot'ma (Fig. 4), Kresttsy, and Bologoe faults serve as examples. The thickness of the Tolbukhino Formation is sharply different on opposite sides of those faults.

The displacement along the Tot'ma Fault at the northwestern wall of the Central Russian Aulacogen were reverse as compared with the Late Vendian. The northwestern wall underwent an uplift, and the thickness in this wall is twice as small as in the southeastern wall (cf. Poshekhon'e and Tot'ma boreholes with the Lezha and D'yakonovo boreholes). The Bologoe Fault, which was clearly expressed previously, probably con-

tinued to exist still in the Tolbukhino time when it limited the zone of maximum subsidence and thickness from the northwest.

In the Middle Cambrian, the Volga–Urals basement block was somewhat subsided relative to the Fennoscandinavian block. Because of this, the axis of the most intense subsidence of the epicontinental basin in the central East European Craton was shifted southeastward as compared with the Vendian–Cambrian boundary.

As previously mentioned, the basin axis plunged southwestward, and connections with the Orsha, Volyn–Podol basins, and the Yapetus paleocean existed. However, the displacements along the Rybinsk Fault gave rise to the subsidence of two local sinks separated by a transverse saddle.

The main provenance of clastic material was located within the Fennoscandinavian basement block including its Karelian segment and presumably in the northeast where the young orogen of the Timan Range is located.

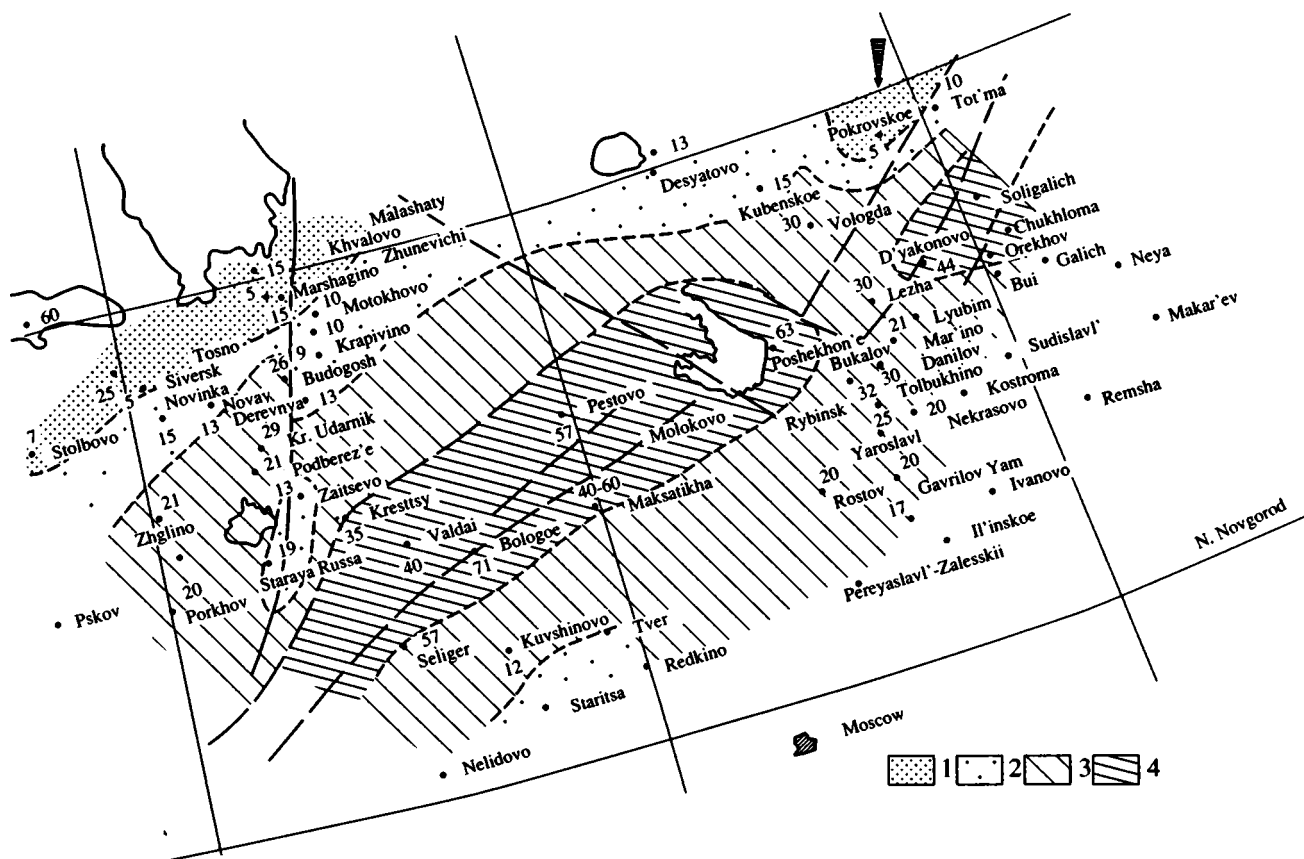


Fig. 5. Structural and facies scheme of the central East European Platform for the Nikolsk time, Late Cambrian. Facies: (1) sandstones, thickness < 10 m, (2) the same, 10–20 m, (3) sandstones and siltstones, 20–40 m, (4) the same, 40–70 m.

THE NIKOLSK TIME (LATE CAMBRIAN)

The sedimentary rocks of the Nikolsk time comprise the Nikolsk Formation of central districts, the lower Ladoga Formation and the Petseri beds in the west of the region (Dmitrovskaya, 1988; Dmitrovskaya *et al.*, 1983).

Everywhere, the deposits of Nikolsk time overlie the Tolbukhino and Sablino formations with a slight erosion at the base. They express a new pulse of the sea invasion into the central East European continent. In the upward section, they are gradually replaced by clayey sediments of the Pestovo Formation (Upper Cambrian), which are preserved from erosion only at restricted areas.

Gray sandstone and siltstone with remains of acritarchs and inarticulate brachiopods are predominant among sediments of the Nikolsk time. Interlayers of dark gray clay and sandstone enriched in gravel occur locally. Three principal facies are recognized: (1) sandstone, 2–20 m thick, (2) sandstone and siltstone, 20–40 m thick, and (3) sandstone and siltstone, 40–70 m thick (Fig. 5).

The facies of sandstone, 2–20 m thick extends as a sublatitudinal zone in the north territory (Stolbovo,

Novinka, Budogosh, Desyatovo, Kubenskoe, Pokrovskoe, Tot'ma, and other boreholes). An isolated field is contoured in environs of Staraya Russa and Zaitsevo settlements. Presumably, it also occurs in the extreme south of the region (Kuvshino, Staritsa, Pereyasavl', and other boreholes). The thickness of the deposits of the Nikolsk time sharply decreases southward, and they were most likely eroded here.

The facies is represented by an inequigranular quartz sandstone with interlayers of dark gray clay in the middle part of the section. The remains of acritarchs, numerous shells of inarticulate brachiopods and their detritus are observed. The feldspar appears as a component of clastic material in the east of the territory (Tot'ma borehole) and some interlayers have reddish tints. The less mature composition of clastic material in the east of the territory may be explained by its supply from the young orogen northeast of the platform rather than from the Fennoscandia. The poor sorting of sediments and the enrichment in clay material are make it possible to classify them as onshore facies of the rapidly spreading sea.

The development of this facies along a submeridional belt extending from the Staraya Russa Settlement to the Zaitsevo Village and further to the Bugodosh and

Krapivno villages is presumably related to motions along the Polotsk Fault. These motions proceeded during the general subsidence of the Novgorod massif, which was previously uplifted in the Tolbukhino time.

The facies of sandstone and siltstone, 20–40 m thick, was most widespread in the basin of Nikolsk time. It is represented by a light and dark gray predominantly quartz sandstone, occasionally with a slight admixture of feldspar (Urdoma borehole).

The sandstones vary from fine- to coarse-grained; most coarse-grained sandstone contains small quartz pebbles and gravel. The sandstones are enriched in clay material to a various extent and embody siltstone interlayers with rare brachiopod shells. The structure of rocks is most often indistinctly bedded and horizontally bedded; cross and wavy bedding with ripples marks occasionally occurs. Fine-grained sandstones and siltstones often reveal traces of intense bioturbation induced by small (2–3 mm in diameter) mud-eaters (Danilovskaya-10, Urdoma-2, and other boreholes).

All sediments bear the indication of their deposition in shallow-water environment and the intense supply of clastic material. The subsidence was most likely completely compensated by a sedimentation. Most coarse-grained sandy rocks with gravel and small pebbles are confined to the area, which was inherited from the saddle of Tolbukhino time (Lezha, Urdoma, and Bukalov boreholes). As previously mentioned, the saddle separated the areas of maximum subsidence. The shoals and temporary islands may be inferred.

The facies of sandstones and siltstones, 40–70 m thick, covers two fields striking in the northeastern direction, which generally coincides with the Orsha–Kresttsy and Central Russian aulacogens separated by the above-mentioned saddle. The prevailing of fine-grained quartz sandstone and abundant siltstones are typical.

Relative deep-water environments of sedimentation are suggested to exist; they were controlled by an enhanced subsidence of grabens, which existed at the place of former aulacogens. Contrasted variations of thicknesses indicate possible movements along the Kresttsy, Bologoe, and Soligalich faults.

Thus, the basin of Nikolsk time was close in its structural pattern to the basin of Tolbukhino time. The difference is caused by more intense input of clastic material and its fast burial resulting in the poor sorting.

As in the preceding epoch, the basin of Nikolsk time was broken up into two local depressions separated by a relative uplift. This probably testifies to the beginning of the structural rearrangement, which was fully developed in Late Cambrian–Early Ordovician when the main axis of the basin changed the plunge direction from the southwestern to northeastern (Dmitrovskaya and Kheraskova, 1997), and the marine transgressions advanced from the opening of the Uralian paleocean rather than from the Yapetus paleocean.

CONCLUSIONS

The conclusions may be stated by the following summary of the history of sedimentation and paleogeography of epicontinental basins in the central East European Craton.

In the Late Vendian and Cambrian, up to the middle Late Cambrian, the marine transgressions came from the western (in present-day coordinates) parts of the platform.

The intensity and timing of transgressions were mainly controlled by structural transformations in the Yapetus and Asian paleoceans. The internal structure of basins and the facies distribution were determined by differentiated motions of basement blocks of the East European Craton.

In principal, the strait-shaped character of basins was inherited from the Riphean rift structure, in particular, from the Orsha–Kresttsy and Central Russian aulacogens.

The removal of clastic material mainly occurred from different segments of the Fennoscandinavian basement block and from the zone of Baikal folding at the northeast of the platform. The supply of clastic material from the Volga–Urals basement block was evident only at the Vendian–Cambrian boundary. Subsequently, this block was probably flooded by a sea or had a lower relief in comparison with the uprising Fennoscandinavian block.

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A Method of Discrimination between Natural and Technogenic Lithochemical Mercury Anomalies in the Aksarai Gas-Condensate Field

N. A. Bogdanov

NPP Ekologo-Analiticheskii Tsentr, ul. Sel'skokhozyaistvennaya 12a, Moscow, 129226 Russia

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Abstract—With the Aksarai gas-condensate field as an example, a method of discrimination between natural and technogenic mercury anomalies in soil has been proposed. The method is based on quantitative relationships between sorbed, sulfide, and isomorphous forms of mercury. The natural lithochemical anomalies trace the deep-seated structure of the gas-condensate field, while the technogenic ones mark ecologically hazardous areas, which are subjected to intense influence of emissions from industrial objects. The method can be applied to prospecting for promising oil- and gas-bearing areas.

The elevated natural background concentrations of S-containing gases, hydrocarbons, and Hg are infrequently observed in air and soils in Hg-bearing ore, oil-and-gas, and gas-condensate deposits (*Khimiya...*, 1995; Pikovskii, 1993). For example, before the beginning of the Aksarai gas-condensate field exploitation and the Aksarai gas-condensate Plant (AGP) construction in 1987, SO₂ and H₂S concentrations several times higher than their average diurnal maximum permissible concentrations (MPC) were noted in air near the Aksarai Settlement in some places above the gas-condensate field dome. The mercury content in the natural gas from this deposit amount to 0.3–2.5 µg/m³, which is an order of magnitude higher than the clarke value for sedimentary rocks. In 1989, the Hg concentration in air, immediately near the AGP, did not exceed 50 ng/m³, while its content in flue gas of the sulfur-producing installation was 180–300 ng/m³ (the height of the installation tube is 210 m). The Hg emission sources also include AGP structure elements, such as high- and low-pressure flares, the boiler house chimney, production wells, and initial gas treatment installations.

In 1990–1991, the automobile mercury-gas survey aimed at an appraisal of the AGP impact on the environment and human health revealed several stable atmogeochemical Hg anomalies, within a radius of 30–50 km from the industrial complex. The metal concentrations were 100–120 ng/m³, which is comparable with technogenic Hg anomalies (up to 150 ng/m³, relative to the average diurnal MPC 300 ng/m³) in Astrakhan (Bogdanov, 1995a). The measurements were carried out at sufficient distances from the local emission sources, when winds at the sampling points were gentle to moderate (4–8 m/s) and oriented toward the AGP. Above the other part of the study area, Hg contents were 25–70 ng/m³. Supposedly, the atmogeochemical anomalies are produced by natural emanations along

zones of deep-seated faults. At the same time, a distribution map of total Hg contents in soils turned out to be low-informative in this respect (Fig. 1). It allowed us neither to validate nor to disprove the data of the mercury-gas survey, nor to identify the Hg accumulation centers as natural or technogenic.

Attempts of such identifications are rare. They were reported only for areas of localization of Hg-bearing ore deposits and were based on an interpretation of the contents of different forms of Hg occurrence in soils (Tauson *et al.*, 1995). From experience and an examination of the available information, we realized that solving problems regarding the discrimination between lithochemical Hg anomalies of different types, and the appraisal of an ecological hazard of the Hg accumulation centers, are related not so much to the level of the total Hg content, as to peculiarities of its behavior and distribution in soils and bottom deposits and, primarily, to a relationship between the Hg forms here. These problems have been unapproached until now.

The purpose of the present work is to substantiate a method of identification for natural lithochemical anomalies of Hg (including its application to prospecting for promising gas-bearing areas) and of their discrimination from technogenic, ecologically dangerous centers of Hg accumulation within aureoles of the total accumulation of this element. This method is based on the relationship between different forms of Hg occurrence in soils in the Aksarai gas-condensate field.

The high-promising gas-bearing area is confined to the Astrakhan Arch of the Sarpa Megadepression within the Caspian Syncline and the associated neotectonic Bukeev Syncline, which are crosscut by a system of deep faults (Fig. 1). The area is situated in lower reaches of the Volga River and in its upper delta and occupies the right and left banks of its valley. Within

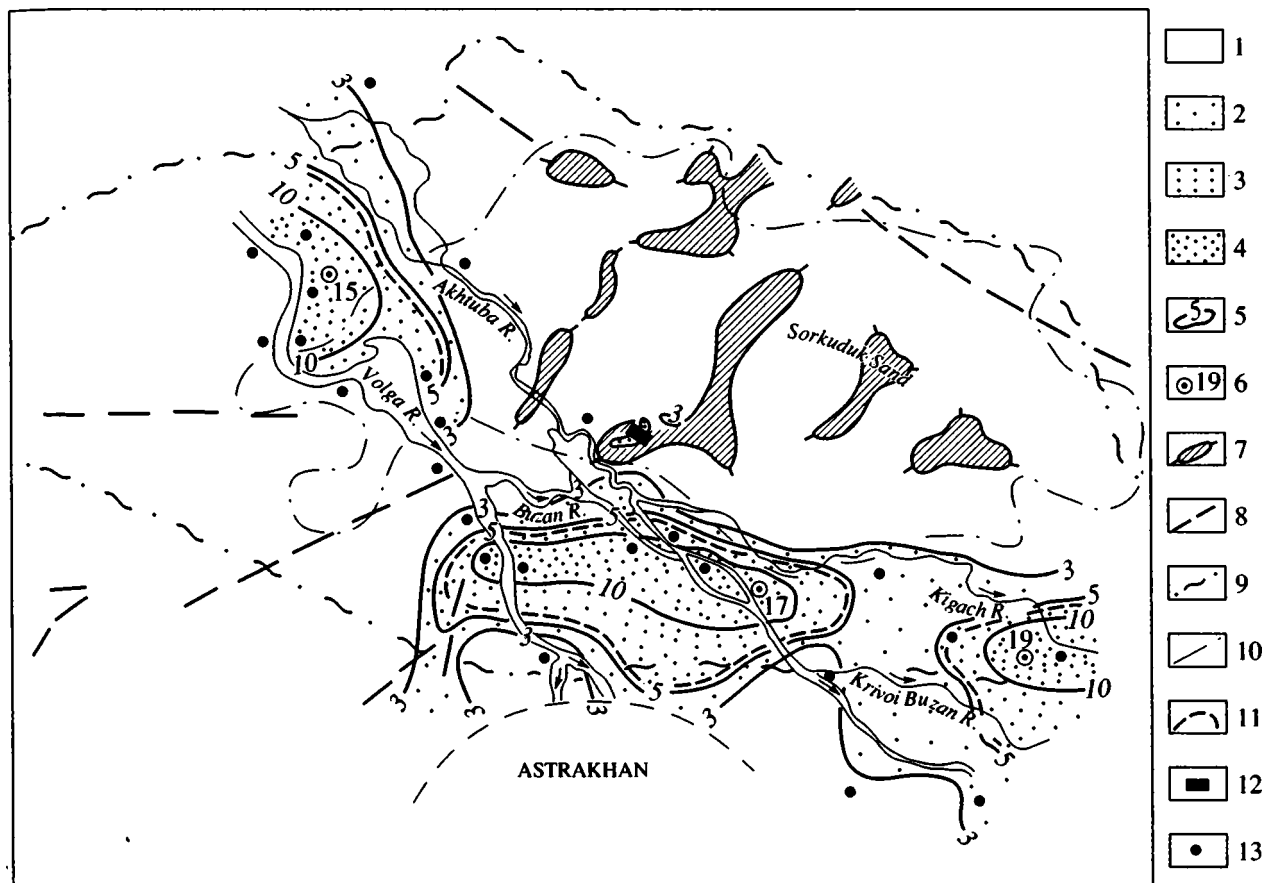


Fig. 1. Distribution of bulk concentrations (C_c) of Hg in soils from the Aksarai gas-condensate field and its schematic structure. C_c values: (1) <3 ; (2) 3–5; (3) 5–10; (4) >10 ; (5) C_c isolines; (6) location of samples with maximum C_c values; (7) salt massifs and domes of the Astrakhan Arch with heights of their tops ranging from 500 to 1000 m; (8) deep faults based on geophysical data; boundaries of: (9) highly promising gas-bearing area, (10) mid-Carboniferous oil- and gas-bearing rocks of the Aksarai gas-condensate field, (11) suburbs of the city of Astrakhan; (12) gas-condensate plant; and (13) populated localities.

the Astrakhan Arch, the tops of salt massifs and domes of mid-Carboniferous oil- and gas-bearing rocks, which are primarily distributed on the left bank, occur at depths of 500–1000 m. Along the axis of the Bukeev Syncline, within the Volga-Akhtuba floodplain, the erosional Volga-Akhtuba Depression is stretched. This depression cuts Paleozoic, Mesozoic, and Paleogene rocks and surrounds the Astrakhan Arch on the east. In the Pliocene, thalwegs of pre-Akchagylian tributaries of the paleo-Volga River were opened onto this depression; subsequently, ingressional marine bays were repeatedly formed here. To the northeast of Astrakhan, the bottom of Pliocene deposits reaches depths of 740–800 m (Obidentova, 1975). Kungurian evaporates are covered with a suprasalt complex of Pliocene-Quaternary and Recent alluvial-marine and eolian sandy-clayey deposits that are enriched in sulfates and chlorides. A gently undulating topography of the Khvalynian alluvial-marine plain is represented by a combination of landscape-subordinated (smoothed) areas of the Volga-Akhtuba floodplain (overgrown with forest belts along watercourse channels) and autonomous

massifs of Baer mounds, which are complicated by hummocky (4–5 m) sandy semideserts on the right and left banks. The study area is characterized by a sublatitudinal orientation of the long axes of wind roses. The climate is dry and hot, and the sunshine duration reaches 2682 h per year.

In the course of the AGP environmental impact appraisal, the investigation predominantly embraced virgin soils ($\text{pH} = 7.2\text{--}8.0$) of autonomous landscape elements. For the top surfaces of the Baer and sandy mounds covered with sandy and sandy-loamy soils, landscapes of the Ca-Na migration class (associated with the salinized and gypsum classes) are typical. Soils of the mounds are characterized by a high degree of the self-cleaning potential. In the Volga valley, landscapes of the carbonate-gleyish (Ca-Fe) migration class with predominantly loamy soils (often secondarily salinized by sulfates) have been most intensely cultivated. Soils of this type are characterized by an elevated capacity for the sorption of pollutants.

In April 1997, soils were sampled within a radius of up to 50 km from the AGP. Within a distance of up to 5 km from the AGP, 75 samples were taken along 10 different azimuthal profiles, in points located at distances of 0.03–0.1, 0.2–0.3, 0.5–0.8, 1, 2...5 km from the plant. Within a radius of 5 to 50 km from the AGP production zone, 59 soil samples were taken along 16 directions at distances of 8–10, 20, 30...50 km. In virgin lands of semideserts, the samples were taken from sectors 50 × 50 m in size, from a surficial (1–5 mm), more or less tightly cemented, sandy crust that was often covered with moss under bushes on the mound tops. In the river valley, preference was also given to the sampling of autonomous elements of the landscape: Baer mound outliers; tops of small, turf-covered dunes; channel banks; etc. When such forms were absent, we chose floodplain areas that were either not flooded during high-water periods or protected by artificial earth bars. The samples were taken from sectors of the above-specified size, from the layer 0–10 cm.

The total Hg content in the samples was determined using an atomic absorption mercury analyzer at the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements (IMGRE). The detectability threshold was 1 µg/kg. Thermal occurrence forms ("thermoforms") of Hg were determined using an IMGRE-900 atomic absorption analyzer with the Zeeman effect. The method is distinguished by an express and selective character of analysis: the material was analyzed without a preliminary sample preparation and regardless of the total concentration level; a continuous sample heating allowed us to clearly separate the distinguished forms from each other, with respect to the sublimation temperature, and to avoid an overprinting of one thermoform onto another. According to the sublimation temperature, the thermoforms had been arbitrarily correlated with principal Hg compounds (Tables 1, 2).

Sources of the Hg supply to soils of the investigated area are represented not only by the emissions from the gas-condensate plant and by the global air mass transfer of pollutants, but by some components of the regional infrastructure as well. These components include the following: (1) emissions from installations (boiler houses, forges, heating systems of private houses, along with motor, railway, and river transport, etc.) using fossil fuel (coal, peat, black oil, diesel fuel, and gas) in populated localities and along transport mainlines; (2) Hg-containing accumulations of industrial and domestic wastes; and (3) residual aureoles of pesticides and fungicides extensively applied in agriculture.

The presence of the intricate system of deep faults determines a real possibility (confirmed by the mercury-gas survey data) of natural Hg emanations at intersections of fracture zones and local dome-shaped structures of the Aksarai gas-condensate field. Therefore, it is very difficult to discriminate natural and technogenic

Table 1. Background distribution of Hg thermoforms and values of indices in biological and geochemical activity of Hg for sandy loam of autonomous landscapes in the northern and northeastern periphery of the Aksarai gas-condensate field, at a distance of 50–70 km from the industrial complex

Thermoforms	Sublimation temperature, °C	Content, %	Background content, µg/kg	C _{ga}	C _{bm}
FR	<180	25	9	0.7	0.7
CL	180–250	16			
PS	250–360	18			
CS	360–400	2			
SD	400–500	16			
IS	500–1100	23			

Note: Hg thermoforms: (FR) free, (CL) chloride, (PS and CS) physically and chemically sorbed, (SD) sulfide, and (IS) isomorphous; (C_{ga} and C_{bm}) coefficients of geochemical activity and biochemical mobility of Hg during its transition from soils to plants.

Table 2. Conventional relationships between the thermoforms and the principal chemical compounds, according to the Hg sublimation temperature (°C)

Hg°, halogens without Cl-, nitrate, acetate, fulminate	Chlorides, methyl- and ethyl-Hg, arsenate		Oxides, sulfates, sulfides (isomorphous)		
FR	CL	PS	CS	SD	IS
0° 180°	250°	360°	400°	500°	1100°

Note: For abbreviations, see Table 1.

aureoles among the total Hg mass in soils. This fact predetermines a necessity to apply not only traditional methods of examination of the metal distribution with the use of the concentration coefficient ($C_c = C_i/C_b$, where C_i and C_b are the element content in a sampling point and the soil geochemical background, respectively), but to apply previously accumulated data (*Khimiya...*, 1995; Tauson *et al.*, 1995) and the method developed by the author of this paper for determining the quantitative relationship between thermoforms of Hg in the substrate (Tables 3, 4). The method is based on well-known features of Hg behavior in the natural environment (*Povedenie rtuti...*, 1989; *Rtut'...*, 1979). These features assume that ecologically dangerous (systematically hazardous) centers of Hg accumulation appear in soils containing geochemically active, unstable (under surface conditions), readily soluble metal compounds.

Metallic mercury and many inorganic compounds of Hg are almost insoluble in water, inert, and poorly absorbed by living organisms. These substances are comparatively easily removed from organisms. The fatal (for plants) level of Hg concentrations in soils is

Table 3. Paired correlations for Hg: total content (C)—thermoform and average content ($\bar{C}$)—dispersion (D) for segments of the soil sampling zone with different intensities of the Hg accumulation, within a radius of 50 km from the gas-condensate plant ($\mu\text{g/kg}$)

1. Areas on the right and left banks of the Volga River, situated at a significant distance from stationary local pollution sources (emissions from motor transport are episodic, because of a sparse system of steppe country roads)

Sandy and loamy soils depleted in humus, $C < 50$, 25 samples

	C	FR	CL	PS	CS	SD	IS	$\bar{C}$	D
C	1							15.2	7.1
FR	0.96	1						4.0	2.1
CL	0.95	0.91	1					2.5	1.2
PS	0.97	0.89	0.93	1				2.5	0.98
CS	0.87	0.80	0.79	0.87	1			0.3	0.1
SD	0.97	0.89	0.91	0.95	0.84	1		2.3	1.05
IS	0.96	0.87	0.86	0.93	0.87	0.95	1	3.6	1.9

2. Floodplain areas with an elevated concentration of local pollution sources, including motor transport on highways and country roads, connecting large populated localities

Humus-rich loamy and clayey soils, $C = 4-279$, 22 samples

	C	FR	CL	PS	CS	SD	IS	$\bar{C}$	D
C	1							118	79.4
FR	0.69	1						22	12.7
CL	0.80	0.57	1					47	44.7
PS	0.60	0.26	0.03	1				23	33.9
CS	0.79	0.57	0.71	0.31	1			1.0	0.75
SD	0.86	0.42	0.84	0.33	0.83	1		12	9.7
IS	0.82	0.47	0.34	0.91	0.61	0.60	1	13	6.8

Note: For the abbreviations see Table 1.

caused both by the capability of plants to selectively accumulate this metal and by the composition, type, and pH of the medium, peculiarities of the source influence, and other factors. An intense absorption of Hg vapors by terrestrial parts of plants is also possible in the course of its sublimation from soil enriched in native mercury or in its readily soluble compounds, which correspond to low-temperature forms (Table 2). Humus-rich substances and loamy soils hold Hg more tightly than humus-poor mineral components and sandy loams (Tables 1, 3). An inactivation of mobile forms is facilitated by alkaline pH conditions and sulfur-containing compounds. However, under the above-described conditions, Hg methylation is possible in floodplain-related silted loamy soils. This process begins at a total Hg content of >0.1 mg/kg in soils or bottom sediments in the presence of organic compounds, which represent donors of the methyl ($-\text{CH}_3$) and ethyl ($-\text{C}_2\text{H}_5$) radicals, and organic (acetic, formic, fulvic, and humic) acids, under neutral and weakly alkaline ($\text{pH} = 6-8$) conditions, at soil surface temperatures of $4-70^\circ\text{C}$, and under ultraviolet radiation (*Po-*

vedenie..., 1989). These conditions are characteristic for some areas of the Volga-Akhtuba floodplain and the delta, where in populated localities and their surrounding are substantially contaminated with oil products which represent potential donors of the above-mentioned radicals (Bogdanov, 1995a, 1995b). Organometallic Hg is distinguished by an increased ability to migrate in a natural environment. It is nearly completely absorbed and very slowly removed from biological objects (*Rtut'...*, 1979).

Investigation has revealed a rather low level of total Hg content in soils within a distance of up to 50 km from the gas-condensate plant. From among 133 samples collected (with Hg contents of $4-279$ $\mu\text{g/kg}$), 71% contain <50 $\mu\text{g/kg}$ of the metal, and only 4% of the samples contain Hg corresponding to $0.5-0.7$ MPC (the MPC level was taken as 0.4 mg/kg, according to the Ministry of Health standard no. 5174-90). The last-named samples were collected from loamy soils at a distance of 5 km from the AGP. The total Hg content in soils within a distance of 5 km from the plant ranges from 4 to 79 $\mu\text{g/kg}$, which is, on the average, 2.4 times

Table 4. Paired correlations for Hg: total content (C)—thermoform and average content ($\bar{C}$)—dispersion (D) in soils from sampling subzones around the Aksarai gas-condensate plant, $\mu\text{g/kg}$

1. Subzone 5 km around the AGP, C = 4–79, 76 samples

	C	FR	CL	PS	CS	SD	IS	$\bar{C}$	D
C	1							23	14
FR	0.91	1						5.5	4.2
CL	0.90	0.82	1					5.6	4.8
PS	0.96	0.85	0.80	1				3.6	2.2
CS	0.89	0.73	0.73	0.91	1			0.4	0.2
SD	0.86	0.63	0.65	0.89	0.89	1		3.2	1.6
IS	0.77	0.55	0.51	0.77	0.82	0.89	1	4.9	2.7

2. Subzone 5–50 km around the AGP, C = 4–279, 57 samples

	C	FR	CL	PS	CS	SD	IS	$\bar{C}$	D
C	1							56	69
FR	0.85	1						11	12
CL	0.88	0.75	1					20	35
PS	0.69	0.47	0.28	1				11	23
CS	0.88	0.80	0.81	0.49	1			0.7	0.7
SD	0.91	0.68	0.90	0.50	0.89	1		6	7.5
IS	0.90	0.75	0.61	0.86	0.81	0.77	1	7	6.1

Note: For the abbreviations see Table 1.

lower than Hg values in soils in the subzone situated within a radius of 5–50 km from the plant. Sandy-loamy soils on the right and left banks of the Volga River, remote from localities of an intense economic activity, contained $\sim 15 \mu\text{g/kg}$ of Hg. This amount corresponds to the background concentration level accepted in 1991 for maps of Hg contamination in the area. The technogenic Hg content in floodplain loamy soils reached, on average, $118 \mu\text{g/kg}$ in more contaminated areas. During the rainy spring of 1997, background Hg concentrations in sandy loams of Baer mounds in the northern and northeastern periphery of the gas-condensate field area were $9 \mu\text{g/kg}$ (Tables 1, 3, and 4). For comparison, the background Hg content in analogous soils near settlements of the Liman and Ikryanoe districts and in sands near the settlement of Sasykoli in the Astrakhan province, were $6 \mu\text{g/kg}$ (Bogdanov, 1995b). This observation is indirect evidence of an elevated share of the natural Hg accumulation in soils, even at a significant distance from the main dome of the gas-condensate field.

The inhomogeneity of provenances, distinct predominance of the technogenic component, and Hg behavior briefly outlined above suggest that it is impossible to discriminate polygenous Hg aureoles only on the basis of total content, even in geochemically homogeneous soils of the autonomous landscapes of ancient alluvial-marine plains. Therefore, we have elaborated

appraisal indices taking into account quantitative relationships between Hg thermoforms.

The *coefficient of endogenous supply* (C_{es}) rather reliably identifies Hg accumulation centers formed due to abyssal emanations along fracture zones of gas-bearing domes. Its application is substantiated by the following considerations. The highest-temperature isomorphous Hg in crystalline lattices of relevant minerals is of natural genesis. Previous investigations revealed a predominance of sorbed (except for chloride) and sulfide forms in samples taken from deep fault zones within areas of Hg-containing ore deposits (*Khimiya...*, 1995; Tauson *et al.*, 1995). The genetic commonness of natural (isomorphous, physically sorbed, and sulfide) thermoforms is also evidenced by our data on close correlations between these forms, particularly, in places of weak anthropogenic influence within the 50-km zone around the AGP (Tables 3, 4). Chemically sorbed Hg is highly dispersed over the area and has minimum average contents ($\bar{C}$) and dispersion (D) among other forms; however, it is closely associated with sulfides and also enters into the distinguished group of natural thermoforms. The curves showing the natural thermoform distribution, as a function of the total Hg, reveal a peculiar threshold of the total Hg content ($50 \mu\text{g/kg}$). Below this threshold, sandy soil samples, collected at a significant distance from technogenic pollution

sources, have a direct correlation to thermoform with the total Hg content. The group of physically and chemically sorbed sulfide and isomorphous (PS-CS-SD-IS) thermoforms, is characterized by very strong correlations (0.81–0.92). The thermoforms are quite evenly dispersed. The difference between the D and $\bar{C}$ values varies within a range of 1.5–3.2 $\mu\text{g/kg}$ (0.2 $\mu\text{g/kg}$ for the chemically sorbed form). Above the threshold value of the total Hg content, the distribution curves are linear (for the chloride forms), parabolic (for the physically sorbed and sulfide forms), or hyperbolic (for the chemically sorbed and free forms). The curve approaches an asymptote for the isomorphous Hg versus the total Hg content. It is important to note the very close (0.94) correlation between contents of physically sorbed and isomorphous forms of Hg, and the weak inverse (–0.1) dependence between contents of physically sorbed thermoform and mercury chlorides (low-temperature varieties of the sorbed forms). Mercury chlorides are practically unassociated with the isomorphous thermoform (the correlation coefficient is 0.15). These correlation features suggest that within this range of the total Hg contents, the physically sorbed Hg belongs to the group of natural thermoforms; in addition, these data are evidence of a genetic heterogeneity of chloride forms of Hg with respect to the physically sorbed and isomorphous (natural) forms of Hg.

The revealed regularities in the distribution of thermoforms allow us to distinguish centers of the natural accumulation of Hg in soils at the expense of its supply along zones of fracturing. For this purpose, the coefficient of the endogenous supply (C_{es}) can be used:

$$C_{es} = \frac{\sum_i (\text{IS, SD, CS, PS})}{\sum_{bg} (\text{IS, SD, CS, PS})},$$

where the numerator represents a total percentage of thermoforms of the natural group for a certain sampling point, and the denominator is the same total for an area of the soil-geochemical background (in our case, $\sum_{bs} = 59\%$). Within an obtained range of coefficient values from 0.4 to 1.5, and for a homogeneous (sandy-loamy or loamy) soil area, $C_{es} > 1$ indicates the presence of an intense natural supply of Hg (Fig. 2). In the proximal subzone, the C_{es} anomalies reflect the structure of the dome of the gas-condensate field; in the distal subzone, as far as could be determined using the prescribed sampling grid density, the maximum intensity of the natural Hg supply is confined to intersections of deep faults in the Sorkuduk Sand Plain and the Malyi Aral Settlement areas ($C_{es} = 1.13\text{--}1.20$). Emanations near the Yasyk-Sakan and Dzhanai settlements are seemingly more intense ($C_{es} = 1.2\text{--}1.5$), because they are related to the loamy composition of floodplain alluvial soils, which hold Hg more tightly than sands do.

However, the deep-seated natural Hg source near the Dzhanai Settlement is more intense ($C_{es} = 1.5$), relative to the Yasyk-Sakan counterpart.

Reliability on the above-specified method of distinguishing centers of natural Hg accumulation in soils is confirmed by a high degree of convergence between the obtained results and data of the mercury-gas survey. Thus, under the relevant directions of gentle to moderate winds, stable atmospheric chemical anomalies of Hg (100–200 ng/m^3) coincided with the soil aureoles of natural Hg emanations along deep fault zones (Figs. 1, 2).

The *technogenic pollution* is characterized by the accumulation of low-temperature free (FR) and chloride (CL) forms of Hg, which have the least constancy and closeness of correlations with the natural group of forms. This conclusion was previously confirmed in (Khimiya..., 1995; Tauson *et al.*, 1995). The centers of the accumulation of predominantly technogenic Hg are revealed using a coefficient that represents the ratio of total content of low-temperature forms to the total content of natural forms in each sampling point. This coefficient can also be used as an *appraisal parameter of the biochemical mobility* (C_{bm}) of Hg, indicating its capacity for transition from soils to plants. The essence of the method is based on a close correspondence of the free and chloride forms to compounds (readily soluble salts of Hg^{2+} , Hg^0 , methyl-Hg and ethyl-Hg), which are most accessible for plants (Povedenie..., 1989). It follows that:

$$C_{bm} = \frac{\text{FR} + \text{CL}}{\text{PS} + \text{CS} + \text{SD} + \text{IS}},$$

where the denominator represents a group of thermoforms corresponding to the most inert compounds hardly accessible for plants. Under background conditions (and close to them), $C_{bm} = 0.7$ (Table 1). In soils within the area studied, the coefficient ranges are $0.2 < C_{bm} < 2.9$. The technogenic influence markedly manifests itself beginning from the values $C_{bm} > 1.0$.

Another appraisal parameter of the technogenic Hg contamination of soils is the *coefficient of geochemical activity* (C_{ga}). The chloride and isomorphous thermoforms of Hg represent peculiar genetic antipodes: the chloride form content indicates the share of technogenic, unstable (under subaerial conditions), readily soluble, geochemically active compounds of Hg in its total content, while the isomorphous form content characterizes the share of inert, natural Hg. This fact is confirmed by very weak or insignificant inverse values of correlations for chloride forms with natural (physically sorbed and isomorphous) thermoforms. Another confirmation is the least, among other forms, correlation between the chloride form and the total content of Hg under the background conditions (Tables 3, 4). Free Hg is released from chloride forms and sulfosalts in the course of methylation and destruction of dimethyl-Hg. These processes are strongly facilitated in settlements due to a certain contamination of soils by oil products

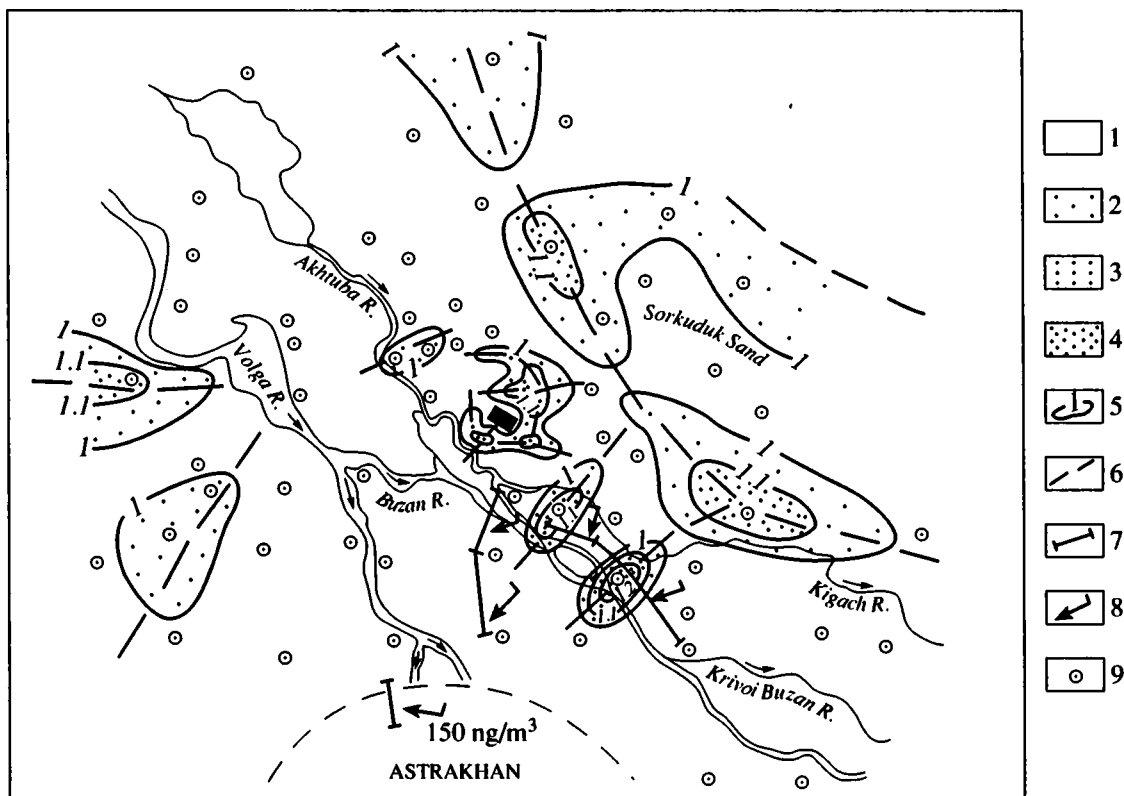


Fig. 2. Distribution of natural lithochemical anomalies of Hg in the Aksarai gas-condensate field, based on values of the coefficient of endogenous supply (C_{es}).

C_{es} values: (1) <1, (2) 1.0–1.1, (3) 1.1–1.2, (4) 1.2–1.5; (5) C_{es} isolines; (6) zones of fracturing, based on the distribution of C_{es} anomalies in the rock substrate; (7) zones of highways, where the mercury-gas survey has revealed atmogeochemical Hg anomalies (100–120 ng/m³); (8) wind direction during the gas-mercury measurements; (9) soil sample locations in the subzone (5–50 km around the plant). Within Astrakhan, Hg concentrations in air are shown as of 1990–1991.

(Bogdanov, 1995a, 1995b; *Povedenie...*, 1989). This indicator of the intensity of soil contamination with technogenic, geochemically active compounds of Hg appears as:

$$C_{ga} = \frac{CL}{IS}.$$

Under background conditions, the value $C_{ga} = 0.7$ indicates a predominance of natural Hg compounds over the technogenic component in the total Hg content. The technogenic component is accumulated by means of atmospheric mass transfer and dispersion. Within the 50-km zone, around the AGP, the C_{ga} value varies within wide limits: $0.4 < C_{ga} < 15.1$. In the proximal (at a distance of up to 5 km from the plant) subzone, an ecologically hazardous, sublatitudinal aureole is situated along the northern periphery of the gas-processing plant (Fig. 3). It represents the proximal zone of concentration of low-temperature mercury compounds emitted by high- and low-pressure flares, boiler houses, and motor transport. The most problematic southwestern aureole is apparently of the same genetic nature. It is related to the precipitation of emissions from the plant, migrating under an influence of gentle N-, NE-,

and ENE-oriented winds. On the left bank floodplain of the Akhtuba River, the Hg accumulation is facilitated by topographic and microclimatic peculiarities of the area, the geochemical barrier represented by a high embankment of the highway, and the proximity of boiler houses in the Seitovka Settlement. Within the remote subzone, the aureoles with $C_{ga} \geq 3$ coincide (in plan) with areas of a possible Hg methylation ($C_{tot} \geq 100 \mu\text{g/kg}$, $C_c \geq 6.7$) and centers with $C_{bm} \sim 2$ (Figs. 1, 3). These compound anomalies, which represent zones of increased and systematic ecological hazard for the vital functions of biological objects, are located near the same settlements where soil anomalies of Hg and other chemical substances were outlined (sums of heavy metals, As, benzopyrene, nitrates, and sulfates): the settlements of Petropavlovka, Novostroi, Rechnoi, and Zavolzhskii, to the northwest of the gas-processing plant; the town of Narimanov to the southwest, the settlements of Volzhskoe, Raznochinovka, and Dzhanai to the south, and the settlements of Teplinka and Algara to the southeast of the plant. In the vicinity of Dzhanai, the aureole contains an appreciable concentration of the natural Hg component. It is obvious that the problematic areas are primarily subject to an impact of local

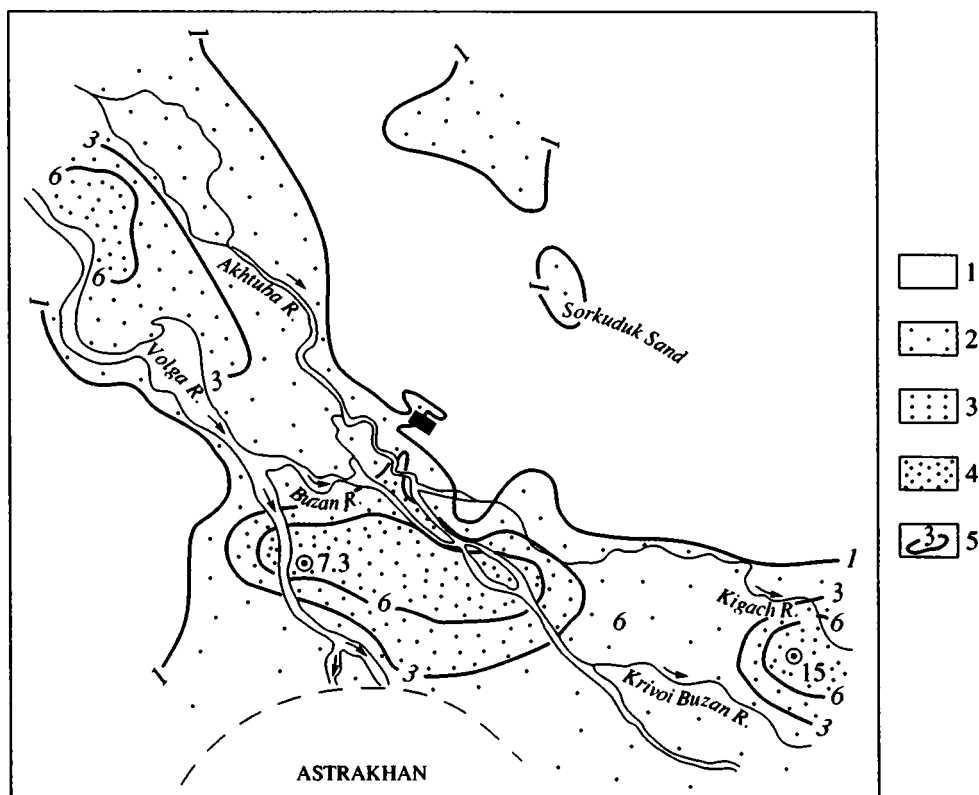


Fig. 3. Distribution of technogenic lithochemical anomalies of Hg in the Aksarai gas-condensate field, based on the coefficient of geochemical activity (C_{ga}).

C_{ga} values: (1) <1, (2) 1–3, (3) 3–6, (4) >6; (5) C_{ga} isolines. For other conventional designations, see Fig. 1.

pollution sources, including Astrakhan, with a certain participation of a vapor–gaseous component of emissions from the tall chimneys of the plant near the ground surface. The influence of such emissions can be excluded only for a narrow local anomaly near the Algara Settlement (Kazakhstan) located at a distance of 50 km from the pollution source. It can be considered that roughness of the topographic surface serves as an unfavorable condition for dispersion and migration of emission products. In the subordinated landscape of the floodplain, the barriers are expressed by a combination of open spaces and forest bands along a branching submeridional system of watercourses. These wind-breaking forest belts facilitate the decreasing velocities of oblique SE-oriented (for example, in the area of Rechnoi and Zavolzhsii) and NW- and NE-oriented (on the Volga–Buzan floodplain) winds. Additionally, under conditions of summer calms or gentle northern winds, local zones of decreased atmospheric pressure above the river valley, which is surrounded by massifs of sandy semidesert, and the general slope of the surface to the south, facilitate a passive mass transfer of the emissions downstream along channels of the delta watercourses.

CONCLUSION

(1) The modern methods of standardization for Hg-contamination of soil, which use only total contents (absolute values, concentration coefficients, and the maximum permissible concentrations), do not allow one to reliably discriminate between accumulation centers of natural and technogenic metal.

(2) The major diagnostic feature of the natural Hg aureoles, which trace emanations along deep fault zones in soil of oil and gas fields, is represented by a group of sorbed (without chloride forms) and sulfide thermoforms and isomorphous Hg. This kind of diagnostic feature is observed in geomorphologically and geochemically homogeneous soil on ancient alluvial–marine plains with numerous technogenic sources of Hg. The principal indicator of the ecological hazard (related to Hg accumulation centers) can be provided by the ratio of chloride and isomorphous thermoforms, which represent peculiar genetic antipodes: the chloride form content indicates the share of geochemically active, predominantly technogenic compounds, while the isomorphous form content characterizes the share of inert, natural Hg. Ecologically hazardous areas, where the methylation of Hg is possible ($C_{tot} > 0.1$ mg/kg), spatially coincide in this region with aureoles of technogenic Hg with the values, $C_c \sim 7$ and $C_{ga} \sim 3$.

(3) The contrasting technogenic Hg anomalies in soil are primarily confined to the Volga River valley and are restricted to areas where numerous settlements and towns are spaced at a distance of 1–5 km or, sometimes, merged with each other. They possess developed infrastructures and include numerous local pollution sources, which have not been accounted for in this investigation. In the cold season, the share of Hg emissions from thermal power installations increase. Chemical pollutants are accumulated in snow during winter and introduced into soil snow melting in spring. This concentration, accumulation, and seasonal dynamics of technogenic Hg are all overprinted on stable natural aureoles of this element.

(4) When the sampling grid is sufficiently dense (tens and hundreds of meters), the C_{es} distribution indicates structural features of gas-bearing domes, while a less dense grid traces zones of fracturing, dome masifs, and promising gas-bearing areas.

(5) A spatial localization of natural soil anomalies related to an endogenous Hg supply is well consistent with the distribution of stable chemical anomalies, which were previously revealed in the near-ground atmospheric layer by the mercury-gas survey. This phenomenon confirms both the earlier proposed assumption of a natural genesis of these anomalies and a correctness of the elaborated method of distinguishing the natural lithochemical centers of Hg, based on relationships between its thermoforms. A possibility of application of this method to detailed prospecting for promising oil- and gas-bearing areas and significantly low cost of the analytical works can provide feasibility of this method under shallow-marine conditions in the northern Caspian Sea as well.

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SHORT
COMMUNICATIONS

Devonian Stratiform Ferromanganese Deposits in Macedonia and Kazakhstan: Comparative Features

I. N. Tomson,* T. Serafimovsky,** O. Spasovsky,** and N. T. Kochneva*

* *Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences,
Staromonetnyi per. 35, 109017 Russia*

** *Faculty of Mines and Geology, Macedonian Republic University, Shtip, 92000 Macedonia*

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Abstract—A brief description of the stratiform iron mineralization in western Macedonia, with the Taimishte ore district as example, is given. It is shown that siderite–chamosite ore layers are confined to Devonian carbonaceous shale horizons, and an admixture of galena, sphalerite, and chalcopyrite is present in ores. The Taimishte ore district is compared with the Atasui ore district containing the Devonian ferromanganese mineralization and associated base metal lodes. This work presents similar and distinctive features of these two ore districts assigned to the Devonian orogenesis.

The Devonian is among active panorogenic periods in the Earth's history accompanied by intense tectonic movements (orogenesis, riftogenesis, and magmatism). According to Leonov (1976), the Devonian activation was characterized by a synchronous orogenesis in different regions of the Earth. The Devonian orogenesis was independent of the Lower Paleozoic history of geosynclines. The Devonian was a highly productive (ore-bearing) period, when several types of mineralization, including the stratiform type, were developed. The cognate iron and manganese specialization of stratiform ores in western Macedonia and Atasui (Kazakhstan) makes it possible to compare these two ore-bearing districts that are characterized by an affiliation to the common Devonian epoch of tectonomagmatic activation, the stratiform type of ores, and the ferromanganese specialization of several deposits.

Below is given a short review of the Devonian stratiform iron mineralization, based on an ore district of western Macedonia where folded Dinaride rocks host a NNW-oriented ferromanganese metallogenic zone with several economic-grade ore districts. The Devonian Taimishte ore district, located to the west from Kichevo in the Krivaya River basin, is an example (Fig. 1). This sector of western Macedonia is mainly composed of Lower Paleozoic rocks intruded by Upper Paleozoic granites. The overlying section consists of Mesozoic terrigenous–carbonate rocks and Neogenic–Quaternary rocks. Paleozoic rocks are divided into two associations. The Cambrian–Ordovician association is composed of a volcanosedimentary sequence of the greenschist facies. The Devonian association, which has a tectonic contact with the older one, includes Devonian fauna and can be divided into three horizons. The subore horizon is composed of phyllite, shale, and sandstone. The ore-bearing horizon comprises graphitic schist, shale, and sandstone with ore layers. The

supraore horizon consists of shale, sandstone, and graywacke. The uppermost section is composed of limestone with the Devonian fauna (Fig. 1).

The ore-bearing horizon includes siderite–chamosite ore layers. The thickness of this horizon varies from 60–100 m at the Zayachka Buka deposit to 200 m at the Darda Kula deposit. The horizon also incorporates graphitic schist and grayish green siltstone grading into chamosite shale and siderite–chamosite ore represented by one to three layers and several thin interlayers. The graphitic schist is composed of the predominant sericite, graphite, and fine-grained quartz, along with the subordinate zircon, muscovite, and pyrite. The Middle Devonian sequence consists of pyroclastic material and rhyolite. The ore district includes abundant Triassic rocks represented by conglomerate, siltstone, sandstone, limestone, dolomite, and diabase.

The structural position of the Taimishte district is governed by the junction of diverse-oriented, extended, linear fracture zones revealed by the space photo deciphering (Fig. 1). The NE-oriented fracture zone stretches across Albany to Debar and Skopje and further toward the Bulgarian border. The ore mineralization is observed along the entire structure. The Krivaya River dome, which hosts the ore district, represents the central sector of a larger ring-shaped structure revealed by the morphostructural analysis and space photo deciphering. The Chaushika, Zayachka Buka, and Darda Kula ore fields are confined to the Krivaya River dome with limbs dipping at 10–20°. One can observe a distinct system of radial fractures connected with the dome. The NE-oriented fracture divides the ore district into two blocks. The eastern block is subsided for 200–300 m.

Layered ore bodies dip at 10–20° and locally are subhorizontal. The ore horizon is subdivided into the upper, middle, and lower layers with thickness varying

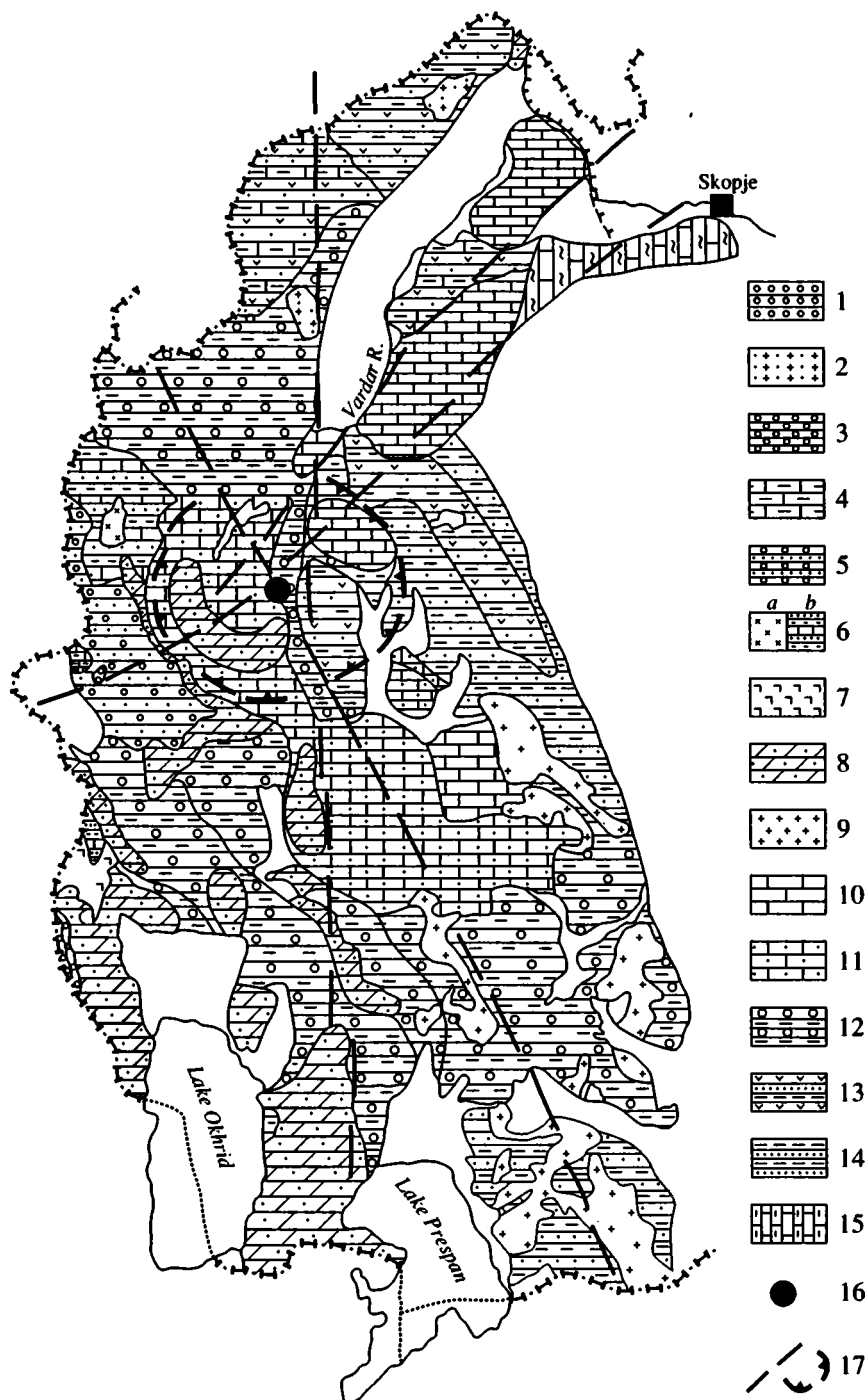


Fig. 1. Structural position of the Taimishte ore district in Dinarides (based on the lithoformation map compiled by N. Dumurdzhinov). Alpide associations: (1) Eocene terrigenous, (2) granitoid, (3) Cretaceous terrigenous, (4) Cretaceous carbonate, (5) Cretaceous flysch-type, (6) Jurassic volcanosedimentary: (a) keratophyre, (b) flyschoid, (7) Jurassic ophiolite, (8) Triassic terrigenous-carbonate, (9) Hercynian granitoid; Caledonide associations: (10) carbonate, (11) terrigenous-carbonate, (12) volcanoterrigenous-ore, (13) spilite-keratophyre, (14) terrigenous-volcanosedimentary; (15) Baikallide undifferentiated association (quartz-sericite schist); (16) Taimishte deposit; (17) linear and ring-shaped structures identified by space photo deciphering.

from a few meters to 90 m (Fig. 2). The dark gray to black, fine-grained (occasionally oolitic), siderite-chamosite ore includes the predominant stilpnomelane and magnetite, the subordinate hematite, apatite, pyrite,

quartz, graphite, and ankerite, and the rare ilmenite, marcasite, arsenopyrite, chalcopyrite, galena, sphalerite, and zircon. Ore layers are embedded in the graphitic schist and sandstone bed with a total thickness of

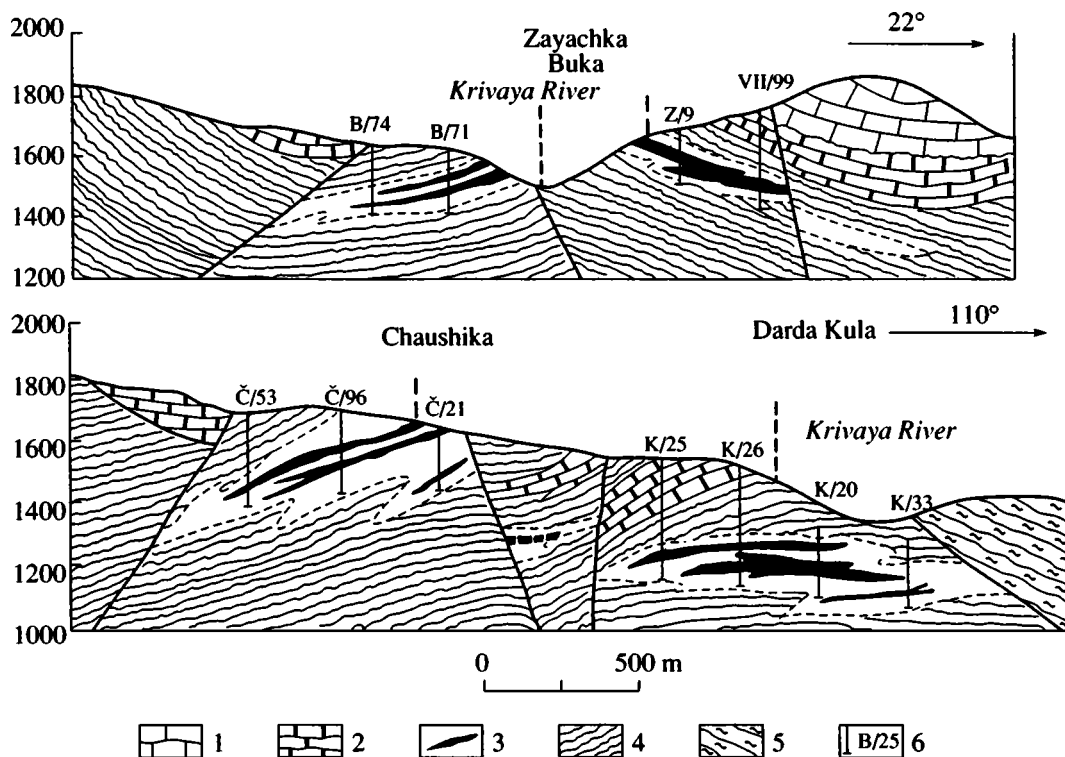


Fig. 2. Geological profiles across the Taimishte ore district. (1) Limestone; (2) marbleized limestone; (3) ore-bearing horizon (graphite schist and sandstone); (4) shale, sandstone, and graywacke; (5) quartz-sericite schist, sandstone, and quartzite; (6) borehole and number.

200 m. The deposits were explored by boreholes drilled along a square grid (35 × 35 m).

In the Kalushka deposit, which was exploited until 1990, the ore contains 36.2 to 47.42% Fe (predominantly Fe^{2+}). Based on spectral analysis, the trace element composition of the Kalushka ore is as follows, ppm: Zn up to 1000, V 20–150, Pb up to 70, Cu 20–250, Cr 80–300, Co 20–110, and Ni 80–900. We can divide this ore into the siderite-chamosite, the chamosite-siderite, and the magnetite-chamosite-siderite types. The iron ore is mainly characterized by the oolitic structure, while the pisolitic or schistose structure is less common.

Macedonian geologists believe that Fe was delivered by hydrothermal solutions during the basic volcanism. This assumption is supported by the presence of pyroclastic material and layered diabase dikes, along with the association of specific trace elements. The presence of terrigenous material and microfauna indicates a hydrothermal sedimentary origin of iron ore. The isotope dating of carbon from ore-associated graphite yielded $\delta^{13}\text{C}$ values ranging from -8.98 to -13.93, suggesting an endogenic nature of carbon.

Secondary geochemical haloes of Pb, Zn, Mo, and Cu confined to the ore-bearing horizon can serve as indirect indicators of a potential sulfide mineralization, as is the case in Kazakhstan. The presence of extensive Mo haloes is generally typical for black shale formations in different

regions. Stratiform sulfide ores are also known in western Macedonia. At the Padalishte deposit, the stratified, 0.5-m-thick, sulfide ore body contains a significant amount of Mo and Ag, in addition to the major Cu and Zn.

For comparison with Macedonian deposits, we give below a brief description of the typical Atasui ore district in Kazakhstan.

The Atasui district is located in the eastern sector of the Caledonian Kazakhstan-Tien Shan massif composed of Cambrian, Ordovician, Devonian, and Lower Carboniferous dislocated rocks (*Gosudarstvennaya...*, 1991). Regional unconformities are mainly registered at the base of Devonian rocks and within the Upper Devonian. All volcanosedimentary deposits of the district are localized within the Zhailma trough. The latter represents a riftogenic depression superimposed on volcanosedimentary rocks of the Devonian volcanogenic belt and Lower Paleozoic siliceous-terrigenous rocks. The Devonian system consists of two different rock associations separated by a regional unconformity. The first association is composed of Lower to Upper Devonian (Frasnian stage) volcanosedimentary sequences. The second association consists of Famennian terrigenous-carbonate sequences (Tomson and Kurchavov, 1995), and is developed in the Zhailma trough. Ore bodies of the Karadzhai, Ushkatyn, Zhairam, and other deposits are confined to Famennian

sequences. According to M.S. Bykova, Famennian sequences include a fine-dispersed, relatively deep-water, sedimentary facies strongly differing from surrounding terrigenous-carbonate rocks (*Gosudarstvennaya...*, 1991). The Famennian volcanism is confined to these rocks. We have also established a cyclic nature of sedimentation. The relatively deep-water, clayey-siliceous-carbonate facies is developed in the middle sector of the Zhailma trough and probably corresponds to a riftogenic zone at the depression basement. This is also suggested by a contrasting difference between the thickness of clayey-siliceous-carbonate rocks (2000 m) and shallow-water terrigenous-carbonate rocks (1000 m). Lower Famennian rocks are devoid of economic-grade mineral concentrations.

Within ore fields, the upper Famennian siliceous limestone is replaced by chlorite-siliceous-carbonate rocks with interlayers of ferruginous jasper and low-grade hematite-magnetite ore. The thickness of ore beds varies from 3 to 50 m. The deep-water rock section is composed of a rhythmic sequence of dark gray, clayey-siliceous-calcareous rocks. The decameter-scale pyrite interlayers contain an admixture of sphalerite and galena. The red-colored limestone includes basic volcanic rocks. The Upper Famennian red-colored member hosts iron and manganese deposits. Devonian rocks are conformably overlain by the Lower Carboniferous limestone.

The Devonian period was also characterized by an intrusive magmatism. Early Devonian intrusive rocks are represented by granodiorite, quartz diorite, and biotite granite. Greisen and tourmaline mineralizations are observed in these rocks. Granitoids intruding the Lower Paleozoic sequence have an absolute age of 388–389 Ma (*Gosudarstvennaya...*, 1991). Late Devonian intrusive rocks are represented by leucocratic granite plutons and veins. Devonian volcanosedimentary rocks represent an orogenic association. Lower Devonian rocks of the basalt-andesite-rhyolite association make up a volcanic belt.

The Atasui ore district is characterized by stratiform ferromanganese and base metal-barite ores formed in two successive stages. Syndimentary ores of this district are believed to be formed as a result of the Famennian exhalative-sedimentary process during a period of 4.5 Ma. Ore deposits are confined to the Zhailma graben-shaped trough. The continuous sequence (600 m) is divided into five sedimentary cycles with a thickness of 12 to 235 m each (Tomson and Kurchavov, 1995). The base of cycles is composed of carbonaceous, clayey-siliceous-carbonate rocks with sulfide (pyrite-sphalerite and pyrite-galena-sphalerite) lodes formed in a reductive environment. Iron and manganese oxide ores are confined to red-colored calcareous rocks at the top of cycles characterized by an oxidative environment. The first (upper Famennian) member of the 50-m-thick, ore-bearing horizon in the Ushkatyn-3 deposit consists of six ore layers with thickness ranging from 1.5 to 8 m. Limestone interlayers between the ore layers are 2 to 10 m thick. Lenticular ferromanganese

ore bodies are extended along ore conduits. The iron ore consists of magnetite, hematite, and siderite, whereas the manganese ore is composed of braunite, hausmannite, jakobsite, and manganocalcite. It should be noted that the iron ore has an admixture of Ge, while the manganese ore contains traces of Tl, Pb, and Zn.

The manganese ore can be divided into the predominant carbonate-silicate and the subordinate oxide, carbonate, oxide-carbonate, and carbonate-oxide types. In addition to the iron ore, the stratiform base metal ore is also developed in certain deposits (e.g., Zhairam, Bestyube, and Ushkatyn).

CONCLUSION

Based on reviews of the stratiform ferromanganese mineralization in western Macedonia and Kazakhstan, we can outline the following common features: (1) the confinement of ore beds to the Devonian sedimentary sequence composed of terrigenous, carbonate, and volcanic rocks of variable composition; (2) the association of ore beds with siliceous-carbonate rocks and carbonaceous shale, which are considered the deep-water facies sediments in Kazakhstan; and (3) the stratified shape of iron ore bodies dominated by hematite, magnetite, siderite, and chlorite.

Differences between the ore districts studied are related to the structure, composition, and age of ores. The mineralization in Kazakhstan is characterized by the following specific features: (1) the confinement to Upper Devonian (Famennian) rocks; (2) the presence of separate stratiform bodies of base metal sulfide ores; and (3) the presence of traces of Ge (20–25 ppm) in the iron ore and Tl (up to 0.1n %) in the manganese ore. In contrast, the mineralization in western Macedonia has the following features: (1) the association with Lower and Middle Devonian rocks; (2) the intricate composition of ore bodies (presence of sphalerite, galena, chalcopyrite, and pyrite, along with hematite, siderite, magnetite, and chamosite) suggesting a sulfide ore potential; (3) the absence of Ge and Tl in ores.

These distinctions can be refined by a more comprehensive study of ore deposits in western Macedonia. Results of the comparative analysis indicate that deposits in western Macedonia can include sulfide ores containing traces of Ge and Tl.

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